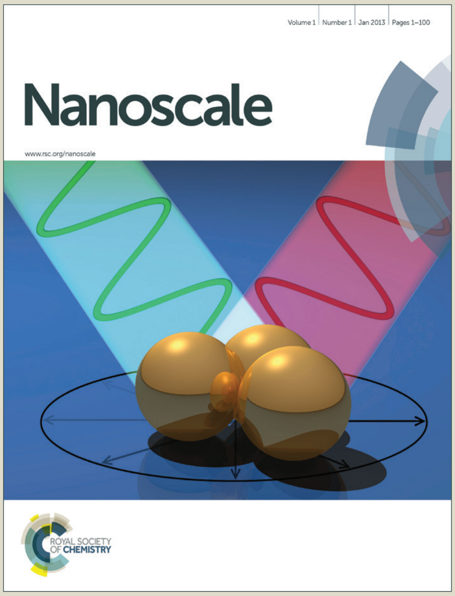
Nanoscale

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

Journal Name

Nanoscale

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Hybrid Materials Science: a promised land for the integrative design of multifunctional materials

Lionel Nicole,[a,b,c] **Christel Laberty-Robert,**[a,b,c] **Laurence Rozes**[a,b,c] **and Clément Sanchez,***[a,b,c]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Since more than 5000 years, organic–inorganic composite materials created by men *via* skill and serendipity have been part of human culture and customs. The concept of "hybrid organic–inorganic" nanocomposites exploded in the second half of the 20th century with the expansion of the so-called "chimie douce" which led many collaborations between a large set of chemists, physicists and biologists. Consequently, the scientific melting pot of these very different scientific communities created a new pluridiciplinary school of thought. Today, the tremendous effort of basic research performed in the last twenty years allows tailor made multifunctional hybrid materials with a perfect control on composition, structure and shape. Some of these hybrid materials have already entered the industrial market. Many tailor made multiscale hybrids are increasingly impacting numerous fields of applications: optics, catalysis, energy, environment and nanomedicine ... In the present feature article, we will emphasize several fundamental and applied aspects of the hybrid materials field: bioreplication, mesostructured thin films, Lego-like chemistry designed hybrids nanocomposites, advanced hybrid materials for energy. Finally, a few commercial applications of hybrid materials will be presented.

Hybrid chemistry history in short

Hybrid Organic-Inorganic Materials (HOIM) are generally described as the combination, at the nanoscale, of an inorganic component and an (bio-)organic one and thus fall within the category of nanocomposite materials. Historically, such intimate mixings were not performed by mankind but have been successfully experienced by Nature over billion years of evolution leading to multi-functional and hierarchical multi-scale systems. [1, 2] It is only very recently, at the geologic time scale, that the first HOIM made by humanity appeared. Due to their high natural availability and their intrinsic properties (high adsorption ability, interesting ion-exchange capacity, and good thermal, mechanical and chemical stabilities), HOIM based on organically modified clays have been part of human existence and were used along history for artistic, societal, environmental, industrial and commercial uses. [3-5] Probably one of the first uses of clays-based HOIM was a long time before antiquity, in the mediterranean region, where clay and soil were mixed with decaying urine to enhance laundry processes. Over the course of human history, the use of hybrid clays spread progressively all over the world. In China for example, hybrid clays permitted to produce very thin ceramics (eggshell porcelain) thanks to the intercalation of urea inside interlayer space which facilitated their further delamination improving plasticity. [6] In America, pre-Colombian civilisations left us, in particular in their frescoes, a well-known pigment, the Maya blue, which was intertwined with their artistic and religious life. This pigment resulted in the incorporation of a natural organic dye (blue indigo) within the channels of micro-fibrous clay (palygorskite). [7, 8] The resulting hybrid is characterised by a strong blue colouring much more stable towards weathering and biodegradation than the fragile indigo dye alone. The stabilisation of the organic dye by the mineral part allows us to admire vestiges 12 centuries old (frescoes, sculptures, codices ...) and thus to know these lost civilisations better.

These first historical examples summarise core principles of HOIM: coupling at the nanoscale of (bio)organic and inorganic components, synergistic effects of this coupling, (multi)functionality, outstanding processability and applicability, strong links with civil society. Over the 20th Century, HOIM had a strong industrial and commercial development. [9, 10] For example, in the 1940s, silicones, hybrid nano-pigments, and a few years' later, organically templated zeolites provided a huge set of functional hybrid materials that have found interest in automotive, aeronautic, construction, medical and paint industries and for catalytic transformations of primary resources in gas and oil. However, the name "hybrid materials" was not mentioned at that time. Mixed organic–inorganic materials nucleated in the middle of 1980s with the expansion of "chimie douce". [11-16] Then the concept of "hybrid organic–inorganic" nanocomposites exploded in 1990s when a pluridisciplinary school of thought was created under the strong impulse of the european actors of the research. [17, 18]

Without any doubt, David Avnir was one of the early pioneers which understood that the mild and versatile synthetic conditions offered by the sol–gel process allow the mixing of inorganic and organic components at the nanometric scale and in an extremely wide chemical composition range and shapes, therefore offering a wide range of possibilities to elaborate tailor-made advanced functional materials. [13] The hybrid materials processed by D. Avnir opened many opportunities in very diverse fields associated to optics, [13, 19-21] catalysis, [22-24] sensors, [25-28] biocatalysis, [29, 30] functional microcapsules [31-38] …. Besides a wide and varied academic career, D. Avnir founded in 1997 with Alon Seri-Levy the Sol-Gel Technologies Company LTD, a society which develops dermatological drug products based on sol-gel microcapsules (see chapter entitled "Commercial applications of hybrid materials"). [31-38]

His work reflects perfectly the increasing development of HOIM during the last 30 years in both academia and industry and their growing implication in our daily life. [9, 10, 39-41] Indeed, the strength of these materials lies in the existence of an extended organic-inorganic interface at the nanoscale and versatile chemical O-I bonds, from weak interactions to strong chemical bonds. [9, 10, 18, 39, 40, 42] Another fundamental characteristic of these materials, which has allowed them a noticeable industrial development, consists in the easiness of their processing fully compatible with existing industrial processes, leading to films, membranes, fibres, powders, monoliths, micro- and nano-patterns. [10, 43-45] The coupling of hybrid materials chemistry with industrial processing methods constitutes a versatile route that facilitates both multifunctionality and device integration. More recently, integrative sol-gel chemistry based strategies allow, the design of hierarchically organised materials from nanometre to centimetre ranges*,* exhibiting additional functionalities and outstanding properties. These multiscale hybrid materials are more and more impacting several fields of applications such as optics, catalysis, energy and nanomedicine. In this short feature article we cannot cover all aspects of the large field of hybrid materials chemistry and the interested reader is referred to some excellent reviews, special issues and books. [18, 39, 40, 46-66] Therefore we will emphasize more particularly our discussions on bioreplication, mesostructured thin films, hybrids nanocomposites designed *via* Lego-like chemistry, advanced hybrids for energy and finally we will describe a few commercial applications of hybrid materials.

Interfaces with soft matter & bioreplication

Nature has provided an astonishing diversity of smart and complex architectures for millions of years. [1, 2, 67] During that period, numerous concepts and vital solutions have been tested through a ‘‘trials and errors’’ strategy resulting in highly optimised biological organisms displaying an impressive ability to adapt to their environment. To this end, Nature has had to manage, with the minimum of materials available and energy expenditure, a set of various vital properties without optimising a single function, what it could be summarised as a compromise between cost and efficiency. Such comprise often results in the presence of controlled disorder at each scale of natural hierarchical architectures. [68-71] In other words, natural architectures are characterised by an average perfection and a multifunctional optimisation. [72] It explains that natural structures are often far from ideal, displaying a structural disorder, which finally strengthens all the properties at the macroscopic scale and which is called "robustness" of effects. [69, 72, 73] At this stage, it is worth mentioning that such lessons from Nature (compromise between cost and efficiency and multifunctions optimisation) are also relevant for the commercial/industrial developments of materials and devices as we will see in the chapter entitled applications of hybrid materials.

These general considerations on Nature could be easily illustrated by natural photonic structures of butterfly wings. [69, 71-73] First of all, a brief description of butterfly wings is necessary since they present several particular features. With regard to the multi-scale structure, a five-level observation method has been adopted to describe butterfly wings (figure 1). [72] The first level is the macroscopic one and concerns the whole wing (centimetre scale). The second level deals with the scales covering wings (roughly hundreds of micrometres). The third level is about striae or ridges on scales (roughly a few micrometres). The fourth level is in the range of 50-100 nm and concerns the structure of striae and inter-striae spacing. The last level is the molecular one and is about the chitinous matrix; this matrix is composed of chitin macromolecules which are organised into microfibrils coated with proteins. Secondly, from a multifunctional point of view, the structure of butterfly wings, besides the main obvious function *i.e.* allowing to fly, participates to several other vital functions such as regulation of body temperature, [74] superhydrophobic and self-cleaning properties, [75-78] and intra- and inter-specific communications (reproduction, camouflage, limited predation ...). And finally, concerning the average perfection of the architecture of butterfly wings, the topological disorder is characterised by variations at each level: thickness of lamellae, inter-lamellae and inter-ridges distances, ridges linearity, deformation and orientation of scales, static and dynamic deformation of wings (figure 1). [69, 72, 73] This multi-scales controlled disorder allows Morpho butterflies to remain blue over a wide range of angles of incidence on the contrary to similar human-made perfect structures. [69, 72, 73]

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

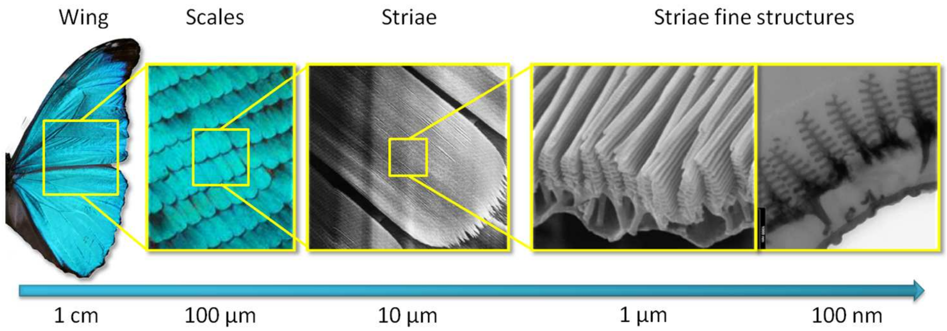


Fig.1 The different scales used to observe butterfly wings and their units of measure [72] (Courtesy of Pr. Serge Berthier)

One of the relevant issues for materials scientists concerning natural and complex architectures is to reproduce such multi-scales structures and their topological disorder with human-made materials. The lack of cost-effective engineering techniques able to produce artificially such hierarchical structures with their optimised imperfections, could explain the growing importance of bioreplication, biomineralisation, biotemplating areas in nanotechnologies. [1, 79] Bioreplication consists in the direct replication of a natural structure and could be achieved *via* either a biomineralisation or a biotemplating approach. Generally, biomineralisation gives rise to a positive or direct (true) replica since natural structures serve as scaffolds, while biotemplating induces a negative or inverse one since natural structures are used as moulds. Various chemical and physical routes have been investigated for replicating butterfly wings including physical vapour deposition (PVD), [80, 81] chemical vapour deposition, [82] atomic layer deposition (ALD), [83, 84] and the most widely studied approach: chemical solution deposition which will be briefly developed below. Since a complete description of the bioreplication topic is beyond the scope of this chapter, the readers are referred to more-specialised reviews. [67, 85-90]

Three main methods involving biomineralisation or biotemplating approaches have been investigated for replicating butterfly wings. Biotemplating of butterfly wings has been performed *via* imprinting lithography [78, 91-94] and sol infiltration [95, 96] methods, and, involves capillarity as the driving force. On the other hand, biomineralisation-based approach has been achieved through a double-step procedure implying first an adsorption step of molecular precursors on the butterfly wings followed by hydrolysis/condensation or nucleation/growth reactions, depending on the chemical nature of molecular precursors. [88, 97-99] It is worth mentioning that this last strategy which leads to positive replica could be viewed as a more or less biomineralisation process depending on both pre-treatment and adsorption steps. In other words, determining the penetration rate of inorganic precursors inside the chitinous structure is not a straightforward issue, especially when the "thickness" of inorganic replica is of the same order of magnitude than the natural fine structure of butterfly wings (below 100 nm). These strategies have permitted the fabrication of numerous replicas of various compositions: $TiO_2{:}Eu^{3+}$, [92] $Y_2O_3{:}Eu^{3+}$, [92, 93] $Pb_{0.91}La_{0.09}(Zr_{0.65}Ti_{0.35})_{0.9775}O_3$, [94] mesoporous SiO_2, [95, 100] TiO_2, [86, 96, 101] ZnO, [102] ZrO_2, [103] SnO_2, [104] Cu-doped WO_3, [105] Fe_2O_3, [106, 107] Fe_3O_4, [107] Bi_2WO_6, [108] CdS, [109] metallic replica (Fe, Co, Ni, Cu, Pd, Ag, Pt, Au) [110, 111] ...

Biotemplating - Imprinting lithography. This approach consists in the coating of the biotemplate with "liquid" materials (polydimethylsiloxane - PDMS [78, 91] or TiO_2-, Y_2O_3- and lead lanthanum zirconate titanate- based wet films [92, 94]) to form a negative replica after a curing step. Once the removal of the biotemplate achieved, the negative mould could be used to pattern another material. This method should be the most suitable technique for the replication of biomaterials at the macroscopic scale since the whole fragile structure of wing is supported by a substrate. However, fine structures of scales are hardly accessible up to now due to low infiltration of highly viscous materials inside the nanometric striae structure of wings which limits the use of this approach to the replication of simple structures located at the upper surface of the biotemplate (figure 2).

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

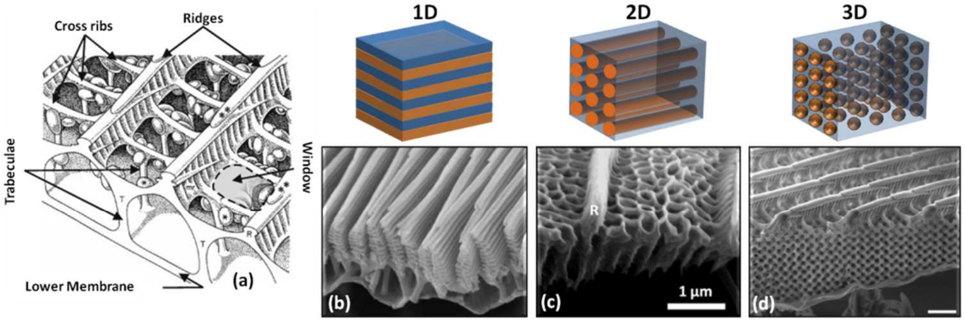


Fig. 2 (a) General drawing of the cross section of a scale (Copyright 2011 Wiley-VCH). Examples of (b) quasi-1D (Courtesy of Pr Serge Berthier), (c) 2D (Copyright 2005 Science) and (d) 3D photonic structures of butterfly scales (Copyright 2011 Royal Society of Chemistry)

Biotemplating - Sol infiltration. This method, initially developed by Galusha *et al.* [112, 113] for replicating beetle scales, has been employed for the replication of butterfly wings presenting a 3D photonic crystal structure (3D PhC). [95, 96] This method implies first a pre-treatment step (ethanol cleaning) in order to eliminate loosely bound proteins and lipids on the wings surface. [95, 96] The pretreated biotemplates were next clamped between two substrates followed by injection of sol-gel precursors solutions at the edge of the assembly. This strategy implies thus to work with highly volatile solvents (such ethanol) presenting a low surface tension and thus a high wetting ability (we have to keep in mind that these natural structures present intrinsically a superhydrophobic behaviour). [78] Moreover, it has been observed that the "sandwich" capillary method limited drastically the excess of inorganic materials around biotemplates, favouring a selected infilling since only the interior of the scale (3D PhC) was filled by the sol and not the upper structure (ridges and cross-ribs - figure 2d). [95] This observation underlines the main advantage of the sol infilling strategy: this approach is self-limited since once air voids are filled by sol-gel materials no more capillary diffusion could occur. However, sol infiltration presents two main drawbacks: *(i)* shrinkage of replicas (which could reach up to 50% of the original biotemplate) due to high temperature treatments required for biotemplate removal and eventually inorganic crystallisation and *(ii)* fragmentation of the macroscopic samples which limits the size of the final materials. Interestingly, a solution limiting the macroscopic fragmentation of replicas and involving sol-gel solution containing surfactant was successfully tested. [95] Besides an improvement of the structural integrity of the replica at the macroscopic scale, this solution led to mesostructured replicas (wormlike mesophase) providing thus a new scale of organisation to the replica compared to the biotemplate.

Biomineralisation-based approach. This approach could be divided in three steps: *(i)* the pretreatment, *(ii)* the adsorption of precursors and *(iii)* the post-treatment. The pretreatment step is of particular importance in this approach since it allows the removal of proteins from natural structures and promotes active side-groups at the chitinous interface, favouring thus the further adsorption and penetration of precursors inside the smallest gaps of the biological structure. After the pre-treatment step, the wings are aged in the precursor solution (anhydrous alcohol or hydro-alcoholic) and then washed-dried. Interestingly this approach could be automated, controlled by computer, allowing thus to increase the thickness of replica by increasing the number of deposition cycles. [97-99] The natural structure is usually removed by a thermal treatment at high temperatures. In order to retain the whole structure of the wing, the thermal treatment is usually performed at low heating rate (1°C/min) with the coated biostructure clamped between two glass substrates in order to keep the coated wing as flat as possible. The thermal treatment results in the crystallisation of the inorganic network of replicas with a size reduction about 50 % due to shrinkage at high temperature (usually above 500°C). Usually performed in air, the heat treatment could be done in reducing conditions leading to magnetophotonic replica (Fe_3O_4) [107] and nanocomposite replica (Fe nanoparticles embedded in a glassy carbon matrix). [110] Interestingly this nanocomposite replica was used as master for PDMS-based imprinting lithography. [110] Alternatively, in the case of metallic replicas, a long immersion at room temperature of the metal-coated scales was performed in highly concentrated phosphoric acid. This alternative treatment was preferred because of the high surface energies of metallic nanoparticles which favour the formation of coarse precipitates at high temperature reducing thus the quality of metallic replicas. [111] This procedure led to full positive bioreplica from the macroscopic to the nanometric scale. Although replicas are rather brittle, they can still be handled with tweezers. Moreover, the thickness of the inorganic replica (below 100 nm) and thus its quality could be adjusted by modifying the concentration in inorganic precursors and the immersing time in the precursor solution. [114] For example, it has been observed that high concentration of inorganic precursors and long immersion time led to the collapse of the fine structure. [108]

Mesostructured thin films

Among O-I hybrid materials, periodically organised mesoporous materials (POMMs) occupy a special place and have been extensively studied for 20 years. [66, 115-120] Historically developed for catalysis, [115] their intrinsic characteristics such as a high surface area, large open porosity, a monomodal narrow pore size distribution, a wide range of the chemical nature of the network (purely inorganic, hybrid, amorphous or crystallised *etc.*), their ability to be doped or functionalised, have allowed them an important development in various domains (*e.g.* separation techniques, sensors, catalysis, fuel cells, batteries, photovoltaic cells, micro-optics and photonic devices, microelectronics, protective coatings, biomaterials, drug delivery *etc.*). [66, 115-119]

Various synthetic routes have been developed leading to POMMs, [66, 115-120] however the evaporation-induced self-assembly approach (EISA) [121-123] appears to be the most convenient pathway for designing efficiently POMMs shaped as thin films, [119] micro- or nano-patterns, [124-126] membranes [127-129] and spherical submicronic particles. [130, 131] Indeed, EISA has demonstrated early a high compatibility with processing techniques commonly used in industry (dip-, spin-, spray-coatings, ink-jet printing, micropen lithography, aerosol-assisted writing process, replica moulding, spray-drying ...), permitting thus the design of POMMs with the most suited shape for a given application. [119, 124, 126, 130-134] The versatility of EISA approach is not limited to the easiness of materials processing. This pathway has allowed the elaboration of numerous materials presenting a wide range of chemical composition (silica-based, non-silica oxides, non-oxides and class I/II hybrid O-I materials) and mesophases (worm-like, 2D-hexagonal, 3D-hexagonal, cubic and lamellar). [119, 131, 135, 136]

Another advantages of EISA, which could be of a great importance for further industrial developments, is related to: *(i)* the intrinsic rapidity of processing techniques which is highly compatible with mesostructuration process (materials shaping and mesostructuration could take place in a few seconds in the case of spray-dried mesostructured submicronic spheres [131, 137] up to several minutes for thin films), [119, 122] *(ii)* the high reproducibility of materials with a perfect control of the stoichiometry of final materials, which is equal to the composition, in non-volatile species, of the initial solution.

However, despite these numerous advantages, several limitations inherent to EISA exist and could hinder a further scaling-up to industrial levels: *(i)* use of flammable and, to a certain extent, non-environmentally-friendly solvents hardly compatible with industrial environment for safety and regulation reasons, *(ii)* (quite long) post-treatment step often implying high temperatures which could be incompatible with some substrates (metals as aluminium alloys, polymers and composite materials) and/or industrial processing (short curing step at relatively low temperature), and *(iii)* final film thicknesses usually limited to several hundreds of nanometres due to the apparition of cracks and delamination during thermal treatment for thicker films.

Two approaches recently reported could circumvent such disadvantage by temporally separating mesostructuration process and film formation: mesostructuration taking place before the complete film formation for the first one and film formation occurring before mesostructuration for the second one. The first one, involving dip-coating at ultra-low withdrawal speed and at moderate temperature (between 40 and 80°C) [138] followed by a simple flash treatment (5 minutes at 500°C), allowed the synthesis of anatase mesoporous thin films from purely aqueous solutions. [139] This simple approach seems to be particularly well-suited for the preparation of crack-free (crystallised) mesoporous thick films through a limited multilayer stacking processing (1.8 µm thick after 4 deposition cycles). However, since the starting solution is purely aqueous, this strategy is rather dedicated to the synthesis of (crystallised) mesoporous thick films from hydrophilic precursors, excepted if micelles are already present in the initial solution, solubilising thus hydrophobic species. The second one, called light-induced self-assembly (LISA), [140-142] is also very attractive since no solvents are required and since the initial solution is stable in the absence of UV light. Briefly, LISA involves an initial solution, composed of commercial poly(dialkoxysiloxane) precursors, amphiphilic block copolymers and a photoacid generator (PAG), which was deposited on a substrate using an automatic film applicator. After the deposition step, the coated substrate was UV-irradiated (2.3 s) at room temperature and at low relative humidity (RH = 30%) resulting in micrometres-thick vermicular mesostructured films. This strategy takes advantage of both non-volatile silica-based oligomers precursors which act as solvent and assure good wetting properties and PAG which triggers inorganic condensation and mesostructuration processes. LISA approach seems to be particularly well-adapted to the fast elaboration of micrometres-thick silica-based mesostructured films and fulfils common industrial requirements.

Considering now the main applications of periodically organised mesoporous thin films (POMTFs), one could observe easily that they are, most of the time, based on their textural properties, implying thus the removal of surfactant. Indeed, the presence of a wide interconnected mesoporous network provides an efficient diffusion of chemical species inside POMTFs and then, an important accessibility towards reactive functions present at their inner surface, leading thus to an exalted reactivity which is a crucial property in a wide range of applications (sensors, catalysis, drug delivery, photocatalysis *etc.*). [119, 131, 143-151]

However, the removal of templating agents, as mentioned previously, could be detrimental in practical applications. Fortunately, surfactant removal is not a prerequisite for the diffusion of chemical species inside such materials. [151-160] First of all, studies dealing with hybrid O-I mesostructured thin films (POMTFs with surfactants) showed that the placement of guest molecules depends on their chemical nature. [161, 162] Indeed, the structure of hybrid mesophases could be divided into three main regions: *(i)* the inorganic framework, *(ii)* the aqueous interface composed of silanols/silanolates, H_2O and polar heads of surfactant and *(iii)* the hydrophobic core of micelles. The localisation of embedded molecules is mainly governed by the "philicity" concept (or "like" dissolves "like"). [163, 164] It means that the solubilisation of lipophilic molecules occurs in the hydrophobic micelle core and the placement of hydrophilic molecules either in the aqueous interface or in the framework. However this tendency does not reflect motion of molecules at the nanoscale. [159] It has been shown that molecules could migrate from the hydrophobic core of micelles towards the aqueous interface (and reciprocally) depending on Brownian motion [154, 159, 165] or chemical reactions (protonation-deprotonation of guest molecules). [28, 166, 167] Moreover, molecular motion is not limited to the nanoscale since a single dye could explore the mesostructure over a wide range in a relatively short time (up to several tens of microns in a few minutes). [153-158] Guest molecules could diffuse inside hybrid O-I mesostructured thin films through *(i)* well-ordered hybrid channels network, *(ii)* defects between adjacent channels, *(iii)* and even at the film top surface (figure 3). [153-156]

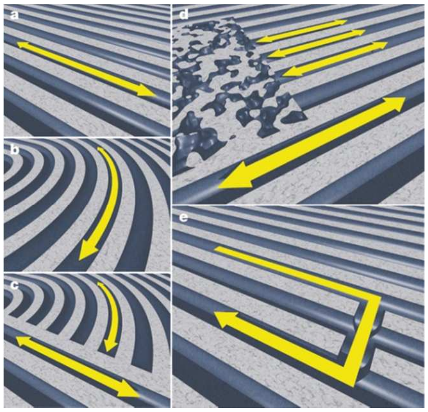


Fig. 3 Schematic drawings of molecular diffusion of a single fluorescent dye inside mesostructured thin film. [155] Straight (a) and curved (b) segments. (c) Domain boundaries forcing molecules to turn back. (d) Molecular travel stopped at less ordered regions. (e) Lateral motion between neighbouring channels (Copyright 2007 Nature Publishing Group).

Numerous parameters could impact the diffusion of guest molecules inside mesostructured thin films: *(i)* for guest molecules: size, charge and hydrophilic/hydrophobic balance of guest molecule, intra- or intermolecular interactions, and *(ii)* for host matrices: type of mesostructure (lamellar, 2D-hexagonale, wormlike, cubic …), pore size, nature of surfactant, amount of silanols/silanolates at the pore surface, amount of water/solvent inside materials, pore surface organically modified or not, pores interconnectivity. [153-156, 158, 159, 165] A general trend about mass transport in mesostructured thin films could be summarised as follows: a molecule will diffuse more easily if weak interactions exist between guest molecules and host matrix. Indeed it has been established that the molecule motion along pores is not continuous and consists in a succession of adsorption/desorption and diffusion events. [153, 157, 159, 165, 168] Briefly, molecules solubilised in the hydrophobic part of micelles (which acts as a solvent) will diffuse faster than molecules in interactions with reactive binding sites at the aqueous interface (silica surface and/or surfactant polar heads). [159, 165] The diffusion of guest molecules could thus be facilitated by a surface functionalisation which aims to hide reactive sites of the pore surface [156, 158] or by increasing the amount of water inside thin films [158, 159, 165] and/or the ionic strength of the aqueous interface (addition of NaCl). [156]

Hybrids by Lego like chemistry

Among the different strategies to design nanostructured hybrid materials, probably the most developed one consists in the incorporation of inorganic nano-objects into organic polymeric matrix. [169-180] The most widely used inorganic nano-components in both academic and industrial worlds are metal oxides and silica nanoparticles and nanoclays. Common features usually improved are mechanical, gas barrier, electrical insulation, flame retardancy properties compared to the unloaded polymer. Besides oxide-based nanoparticles and nanoclays, other inorganic nano-objects such as oxo-clusters, polyhedral oligomeric silsesquioxane (POSS), nanoMOFs, quantum dots have been also investigated. [44, 170, 181-185] Whatever the nature of inorganic nano-objects, the crucial point is to achieve a dispersion of individual nano-objects as high as possible into the polymer matrix. In this sense, the high versatility and the control of surface chemistry of well-defined oxo-clusters offer great potentialities for the elaboration of advanced materials or hybrid assemblies.[60, 62, 186] Hence, the aim in the chemical design of ‘‘Lego-like’’ hybrid systems is to prepare clusters bearing organic surface functionality that create a compatible interface between the organic matrix and the inorganic component.

This section will report first on the versatility of the hybrid architectures that could be obtained with clusters. In a second time, the nature of the links at the hybrid interface will be discussed. Next, the accurate monitoring of nano-building blocks functionalisation will be presented in agreement with the requirement of the organic matrices synthesis. Finally, the more relevant properties of the resulting hybrids will be presented.

Clusters-based Hybrid architectures. The use of clusters in the build-up of hybrid materials allows perfect control of the number of functional groups for further reactions this is difficult to control with nanoparticles. The types of architectures that can be achieved depend on the cluster functionality. The simplistic solution consists of the polymerisation of classical monomers in the presence of the inorganic building blocks bearing unreactive groups. Alternatively, the inorganic component can be introduced into a prepared polymer matrix by physical mixing. This method produces class 1 materials, where clusters are just embedded in a polymer phase without strong interactions between the polymer matrix and the nano-building block (figure 4a).

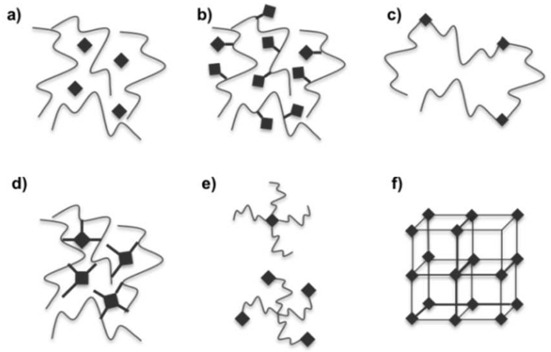


Fig. 4 a) embedded NBBs in polymers b) linear polymeric backbones with pendant inorganic domains nanobuilding blocks formed with NBB which bear one functional group as a single double bond c) linear block copolymer from difunctional NBB d) three-dimensional hybrid networks made from multifunctional NBBs which crosslink macromolecular chains e) star-like architecture (divergent or convergent approach) f) crystalline highly porous three-dimentional networks

Therefore, nanocomposite materials based on a hybrid organic-inorganic network, in which tungsten heteropolyoxometalates

$[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{3-}$, $[W_{10}O_{32}]^{4-}$ are entrapped have been synthesised with electrochemical and photochromic properties.[187] Also reported, the organically modified metal oxide clusters $[Ti_6O_4(C_6H_5COO)_8(OR)_8]$ (R=Et, Pr^n, Bu^n) dispersed in ORMOCER® matrices, which lead to a homogeneous, photo-patternable hybrid system with matching refractive index.[188]

In order to increase the cluster/polymer ratio without aggregation, preparation of class 2 hybrid materials can be promoted by the copolymerisation of an organic monomer, with the nano-building blocks bearing the same or similar functional groups at the surface of the inorganic oxo-core. Depending on whether the species has one or several polymerisable functional groups, it can become either a pendant group[181] (figure 4b), part of the polymer chain[189-191] (figure 4c) or a cross-linker. Furthermore, the building units may also act as polymer initiators, and can form star shaped hybrid architectures[192-194] (figure 4d). Nano-building blocks, such as $RSi(C_6H_{11}Si)_7O_{12}$ (with R: styryl, 3-propyl methacrylate, or 2-ethylnorbornyl) which all bear a single double bond, yield upon polymerisation to linear polymeric backbones with pendant silsesquioxane cubes.[181] From difunctional NBB, hybrid organic-inorganic alternated block copolymers of general formula $[BuSn_{12}O_{14}(OH)_6[OOCCH_2(OCH_2CH_2)_nOCH_2COO]_m$ processed as coatings have been elaborated.[195] Titanium and zirconium oxo-based clusters demonstrate the ability of multifunctional nano-building blocks to polymers crosslink efficiently. [196-198]

Another type of inorganic-organic hybrid materials based on metallic oxo-cluster is crystalline metal-organic framework structures which are obtained by coordinating multifunctional organic ligands to cluster units. [60] Cluster-based networks are a sub-class of metal-organic framework (MOF) structures where clusters are expanded connectors or secondary building blocks (SBU). Yaghi *et al.* [199] reviewed 131 transition-metal carboxylate clusters which are potentially building blocks for MOFs. This compilation of the geometries of building blocks, with different compositions, structures and connectivities, shows the great ability of this approach for the construction of cluster-based metal organic framework structures (figure 4 e). [200]

Clusters-based hybrid interface. In addition to the type of architectures, the nature of the hybrid interface, *i.e.* the nature of the link between the organic matrix and the inorganic nanbuilding block can be tuned from covalent bonds to ionic bonds via iono-covalent bonds (figure 5).

As for sol-gel derived and the other types of hybrid materials, silicon is likely the most studied element in NBB-based hybrid materials. Because of the hydrolytic stability of the Si-C bond, silicon offers a very large variety of organic functionalisation yielding to class 2 hybrids with covalent bonds located at the interface (figure 5a). The $RSiO_{3/2}$ backbone may be readily prepared, from random polymers through ladder polymers to more highly ordered discrete molecular species with the general formula $(RSiO_{3/2})_n$ where n is commonly 6, 8, or 18. These nano-building blocks have become known as polyhedral oligosilsesquioxanes and the name POSS has been trademarked by Hybrid Plastics. [10] Significant applications have been found in polymers and in nanocomposite materials, which have been reviewed extensively.[181, 201] Polyoxometalates POMs, formed by transition metals in high oxidation state (W^{VI}, Mo^{VI}) surrounded by oxo-ligands afford unsaturated organic groups can thus be attached to the cluster core through W-O-Si-C covalent linkages.[202] Jointly, tin shares with silicon a M-Csp$_3$ bond that is stable with respect to nucleophilic agents. These bonds offer strong covalent links between tin-oxo clusters and functional organic moieties. The $[BuSnO(O_2CC_6H_4NH_2)]_6$ cluster, exhibits on its periphery six amino groups amenable to subsequent reactions. It can be functionalised, via reaction with $OCN(CH_2)_3Si(OEt)_3$, to yield quantitatively a dendrimer-like compound with peripheral ethoxy functions.[203] Another interesting tin nanobuilding block is the oxo cluster $[(RSn)_{12}O_{14}(OH)_6]X_2$. This cluster can be assembled through organic networks by using the covalent interface provided by the Sn-C bond[204] or by using the ionic interface associated to the charge compensating anions X (figure 5b). The macrocation can be functionalised with 2-acrylamido-2-methyl-1-propanesulfonate (AMPS), affording nanobuilding blocks with two polymerizable groups.[205-207] The direct homopolymerisation of such functionalised oxo-hydroxo butyltin clusters was successfully performed. $[(BuSn)_{12}O_{14}OH_6](AMPS)_2]$ can also be copolymerized with vinylic monomers to produce gels with ionic interactions at the hybrid interface that are responsible of reversible cross-linking of the organic polymers.

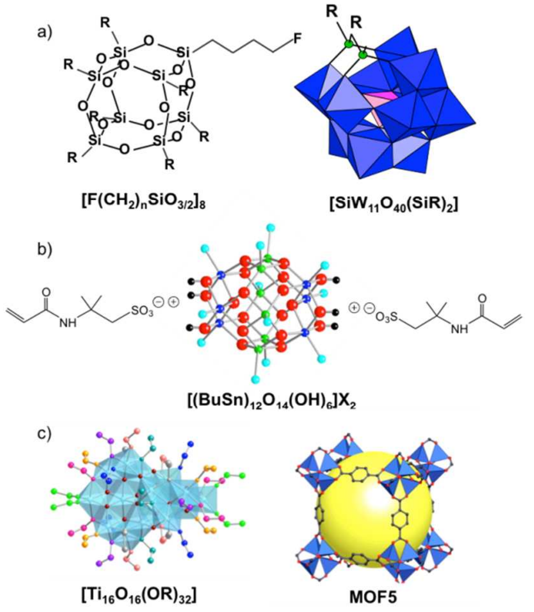


Fig. 5 a) covalent interface with POSS and POM; b) ionic interface with $[(RSn)_{12}O_{14}(OH)_6]X_2$; c) ionocovalent interface with Ti or MOF.

Employing other types of inorganic clusters, especially those of the transition metals, can considerably broaden the range of properties and potential applications. With transition metal cluster the links at the hybrid interface have an iono-covalent character (figure 5c). The functional groups can either be introduced during a cluster ‘‘one pot synthesis’’ or grafted on to a pre-formed cluster. The first method has been successfully used to generate a variety of carboxylate and β-diketonates-substituted metal-oxo clusters. This includes monometallic clusters of Ti, Zr, Hf, Nb and Ta of various shapes as well as mixed-metal Ti/Zr(Hf) or Ti/Y oxo-clusters.[186, 198, 208-216] Clusters with different sizes and shapes and different degrees of substitution can be obtained by varying the metal alkoxide/carboxylic acid ratio and the kind of alkoxo groups of the metal alkoxides. As for carboxylate derivatives, the hydrolysis and condensation reactions of β-diketonate substituted titanium[217, 218] and zirconium[219] alkoxides are used used to prepare metal oxo-clusters. Derivatives by reaction with phosphorus based acids has received much less attention than the reactions of $Ti(OR)_4$ with other complexing ligands (carboxylic acids or β-diketone), but there are some promising results especially with phosphonic and phosphinic acids.[220, 221]

On the other hand, the post-modification of well-defined preformed nano-building blocks offers the possibility of real control over the design of new hybrid architectures. Nevertheless, the post-modification approach requires labile surface organic groups, and simultaneously balancing charge and coordination number during substitution of these groups. Post-synthetic exchange of non-functional ligands against functional ligands is reported by reaction of $[Ti_{16}O_{16}(OEt)_{32}]$ with 2-hydroxyethyl-methacrylate or vinylphenol resulted in a selective and controlled exchange of the ethoxo groups, and $[Ti_{16}O_{16}(OEt)_{24}(OCH_2CH_2OMc)_8]$[196] or $[Ti_{16}O_{16}(OEt)_{32-x}(OC_6H_4CH{=}CH_2)_x]$ (x = 4, 8, 16)[197] was obtained. A manganese oxide cluster with polymerisable carboxylate ligands was also prepared by exchanging the acetate ligands in $[Mn_{12}O_{12}(OOCCH_3)_{16}]$ against acrylate or methacrylate.[222, 223]

For cluster-based MOF structures, the synthesis strategies differ also by the clusters synthetic pathway. The first relies on "one pot" formation of the cluster units, while the second exploits preformed clusters as SBUs. [224] In this second approach, clusters with monofunctional ligands bonded to the surface atoms are employed, which are then exchanged by the bi- or multifunctional linkers to connect the cluster units without loss of its integrity with each other. Such approach can be illustrated by the iron(III) acetate $[Fe_3O(OAc)_6L_3]X$ cluster. When the iron cluster reacts with dicarboxylic acids, acetic acid is liberated and the MOF structure (MIL88) is produced with retention of the trinuclear cluster units.[225] More recently, the exchange of the methacrylate ligands against muconate or terephthalate ligands of the cluster $[Zr_6O_4(OH)_4(OMc)_{12}]$ results in the formation of a porous network with retention of the cluster units.[226] Despite the versatility of structures encountered in titanium oxo-clusters, the formation of 3D hybrid solid from established titanium inorganic brick connected by organic linkers has never been demonstrated. To date, the only highly porous MOF constructed from titanium-oxo-clusters and dicarboxylate linkers reported is denoted MIL-125 with the formula $[Ti_8O_8(OH)_4(OOC\text{-}C_6H_4\text{-}CO_2)_6]$. The octameric SBUs of metal octahedral was never been encountered in three-dimensional MOFs before and never in titanium oxo-clusters chemistry. It was however found previously in a molecular chromium(III) hydroxoacetate. [227] Nevertheless, isostructural NH2-MIL-25(Ti) or with mixed aminated/non aminated-linkers, have been performed by the substitution of terephtalate ligands by amino-terephtalate ligands. [228, 229]

Generation of weak interactions between organic and inorganic NBBs has been also investigated. An approach combining inorganic NBBs and supramolecular interactions, designing by a titanium oxo-cluster $[Ti_{16}O_{16}(OEt)_{32}]$ modified by hydrogen bond acceptors and a telechelic PDMS with two hydrogen bond donors has been recently published.[230] With simple components, it has been demonstrated that well-chosen supramolecular interactions can be used to obtain new hybrid dynamers having the intrinsic properties of the inorganic component (such as photochromism) and improved mechanical properties, due to the supramolecular cross-linking of the polymer chains.[230] A ligand exchange using thioether, $HO(CH_2)_4SCH_3$ results in the successful thiofunctionalisation of the $[Ti_{16}O_{16}(OEt)_{32}]$ cluster.[231] High resolution XPS and STM (Scanning Transmission Microscopy) demonstrated that the sulfide-functionalised cage, $[Ti_{16}O_{16}(OEt)_{24}(O(CH_2)_4SCH_3)_8]$, underwent connection to Au surfaces, forming a monolayer of adsorbed species in which the molecular integrity had been preserved.

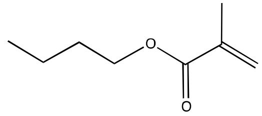
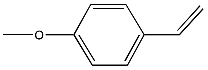
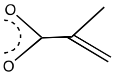
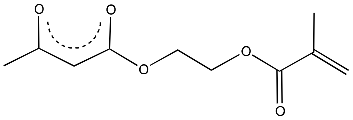
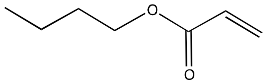
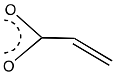
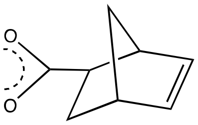
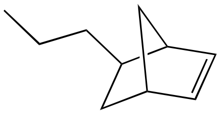
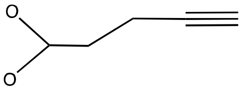
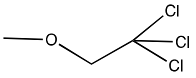
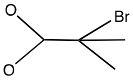
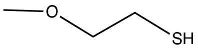
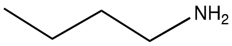
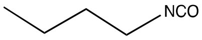
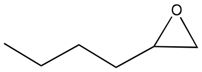
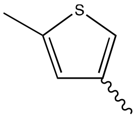
Clusters's functionality. The organic functionality through the organic ligands should be managed in agreement with the polymer formation. Most cluster-based hybrid polymers were prepared by free-radical polymerisation of (meth-)acrylate or styryl-substituted metal oxo clusters and organic co-monomers. It was shown, however, that other polymerisation reactions can be applied as well, provided that the cluster ligands have suitable functionalities. Some functionalities encountered in the literature are summarised in table 1. Clusters containing strained-ring unsaturated ligands were employed in ring-opening metathesis polymerisations,[214, 232] clusters with 4-pentynoate ligands for alkyne-azide click reactions,[216] 2-bromo-iso-butyrate- or trichloroethoxo-substituted clusters as initiator for atom-transfer radical polymerisation,[192-194] clusters with 3-mercaptopropionate ligands for thiol-ene reactions,[215] and polyoxometallates modified by aminopropyl silane for the preparation of cluster-crosslinked polyimides.[233] Cluster-based extended networks were also prepared by oxidation of the $[W_6S_8]$ octahedral tungsten clusters functionalised with thiophene derivatives.[234]

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 1 Some organic ligands for further polymerisation

Organic ligands		**Polymerisation**
   	 	Free radical polymerisation
		ROMP
		Click reaction
		ATRP
		Photothiol-ene polymerisation
	 	Polyaddition
		Oxidative polymerisation

Impact on the properties: from mechanical properties to multifunctional materials. Most of the cluster-based hybrid polymers are highly crosslinked, even when small cluster proportions are employed, because of the large number of reactive ligands. The materials properties of cluster-based polymers do not depend only on the polymerisation conditions and the cluster proportion, but also on the cluster nature.

Some properties are distinctly different to that of the parent polymers and are brought about by the clusters acting as multifunctional crosslinkers as well as inorganic (nano)fillers. Property changes include: (i) cluster-crosslinked polymers are no longer soluble in organic solvents, but swell instead, as expected for crosslinked polymers, (ii) thermal stability is higher compared with the native polymers, (iii) thermomechanical properties are improved and mechanical properties (strength, hardness, brittleness, scratch resistance, etc.) are changed.

Less exploited option is to combine these property changes with properties that are inherent to the cluster, such as special magnetic,[222, 223] dielectric properties,[235] redox[189, 236] or optical properties as refractive index[188]. As an example, fabrication of optical transparent polyimide hybrid films with ultra-low dielectric constant (k = 1.22) has been proposed based on the basis the copolymerisation of an organically modified POM clusters that are incorporated into polyimide chains.[233] Synthesis and characterization of magnetic organic-inorganic nanocomposites based on the $[Mn_2O_{12}(CH_2C(CH_3)COO)_{16}(H_2O)_4]$ building block have also been proposed.[222, 223] Organic–inorganic hybrid materials based on the copolymerisation of the methacrylate-functionalised chromium–nickel wheel with methyl methacrylate $[(n\text{-}C_3H_7)_2NH_2]\text{-}[Cr_7NiF_8(O_2C_4H_5)_{16}]$) present interesting dielectric material for application in microelectronic devices.[235] $[Ti_{17}O_{24}(OPr^i)_{20}]$ clusters functionalised with catechol and isonicotinic acid have been proposed as models for the sensitizer/ semiconductor interfaces in dye-sensitized solar cells.[237, 238] Catalysis properties are exemplified by a series of new di-, tri- and penta-nuclear titanium oxo-clusters prepared with bidentate ligands (2,2′-biphenol and 1,1′-binaphthol). Some of them were found to be effective catalysts for the formation of phthalate diesters. [239]

If a multitude of functional hybrid materials with a very large set of structures, textures and chemical compositions have been described, less attention is paid on cluster based hybrid materials. Nevertheless, the modular approach, from nano-bricks to macroscopic networks, presents a number of advantages. The step-by-step development of the material allows better control over structure on the mesoscale. Prefabricated nano-objects often show reduced reactivity compared to that of molecular precursors; the inorganic component is monodisperse allowing for the development of more well-defined structures, facilitated characterization and an enhanced quality, especially high optical transparency in the final material. But the most important highlights are to combine the wealth of properties proposed by the polymer chemistry with well-defined architectures and specific hybrid interfaces encountered in oxo-clusters to design novel class of hybrid materials. Applications can be suggested for the elaboration of materials with high optical transparency for optics (photochromism, electrochromism or refractive index matching) or adaptive materials (shape memory or self-healing). For this last purpose, a broad range of self-healing materials has emerged over the last decade.[240-242] Such systems, when they have been damaged, heal themselves either spontaneously or with the aid of a stimulus. Several of these materials draw their inspiration from the design of biological materials.[243] As an example, the bio-reparation of mussel byssal threads proceeds by the reconnection after damage of sacrificial cross-links constituted by clustered distribution of catecholato-iron chelate complexes distributed in a polymeric scaffold. [244, 245] Different approaches to built self-healing polymers have been described.[240-243, 246, 247] Especially, repeated healing processes can be achieved with systems based on reversible systems, that either uses covalent [248, 249] and non-covalent bonds, mainly involving bioinspired strategies based on supramolecular chemistry with hydrogen-bonding or metal coordination chemistry. [230, 250, 251] In addition, self-healing materials have been designed by hybridization of polymers with structurally well-defined nanobuilding units. The controlled design of cross-linked poly(*n*-butyl acrylate) (pBuA) has been performed by introducing a very low amount of a specific tin oxo-cluster. [252] Sacrificial domains developed at the hybrid interface and involving ionic bonds play a double role. Indeed, ionic interactions are strong enough to cross-link the polymer, which consequently exhibits rubber-like elasticity behaviour and labile enough to enable, after a severe mechanical damage, dynamic bond recombination leading to an efficient healing process (more than 75% of recovery of the mechanical properties). The strategy is based on the preparation of elastomeric nanocomposites from a cheap and common organic monomer copolymerized with metallic oxo-clusters. Indeed, the small size of the inorganic component and the elastomeric behaviour of the host matrix have been selected to facilitate matter transport towards the damage site. Moreover, to reach the expected property the fine-tuning of the nature of the hybrid interface is achieved by the choice of organic ligands, which surround the metallic oxo-core of clusters based on ionic interactions as sacrificial cross-links in order to prepare dynamic systems and facilitate the subsequent reconnection of local bonds after damage at the mesoscale, which results into a macroscopic effect. [252]

Advanced hybrids for energy

Hybrid organic –inorganic materials have attracted wide attention because of their potential to combine desirable properties of different nanoscale building blocks to improve both mechanical and transport properties. These strategies have been mainly used to develop composite polymer electrolytes for use in lithium batteries [253, 254] and fuel cells.[255]

Progress in ***Li-ion batteries*** relies on replacement of the conventional liquid electrolyte by an advanced solid polymer electrolyte.[256] The PEO–LiX membranes that consist of poly(ethylene oxide)–based (PEO–based) solid polymer electrolytes combined with a lithium salt meet in principle the main requirements (*i.e.* low cost, good chemical stability, and safety) as efficient electrolyte separators. Unfortunately, the ionic conductivity of the membranes remains at high levels only at temperatures above 70 °C and this is the main issue which has so far prevented their wide practical use. More importantly, the conductivity is due to motion of the anion (the lithium transference number is generally low, of the order of 0.2-0.4) and often result in concentration polarization that limit the power of the battery. Many studies have been carried out to overcome these drawbacks.

Some progress has been achieved by dispersing within the polymer matrix nanoparticle ceramic fillers, such as TiO_2, Al_2O_3, and SiO_2. [256] Literature data reported that the role of the ceramic fillers is multiple. Ceramic fillers act as a solid plasticizer for PEO, by inhibiting chain crystallisation upon annealing in the amorphous state at 70°C. [257, 258] It promotes an enhancement of the lithium–ion transference number. [259, 260] Enhancement has been proven by many laboratories and depends on the chemistry of surface state. This behaviour has been demonstrated through experiments performed with sulfate–promoted superacid zirconia (S–ZrO_2) ceramic filler, having a high density of acidic sites (both Lewis and BrØnsted type) at the surface of the oxide.[261, 262] The obtained hybrid organic–inorganic membranes exhibit unique transport properties, as the transference number is 0.81 ± 0.05; that is, a value almost 100% greater than that of the ceramic-free electrolyte (0.42 ± 0.05) (see figure 6). [262, 263] The improvement of the performances is also demonstrated on the properties of full devices. Comparison of cells containing the $PEO_{20}LiClO_4$ electrolyte with and without S–ZrO_2 indicates that cells containing hybrid organic–inorganic separator exhibit a higher cycling capacity, a lower capacity decay upon cycling and in particular, a more stable charge–discharge efficiency. This point highlights a less reactive lithium–electrolyte interface which is favourable for long–term use.

The design of hybrid organic–inorganic membranes allows widening the useful range of temperature but, not yet to a level that make the PEO–LiX membranes suitable for batteries expected to the ones operating at ambient and sub-ambient temperatures. These hybrid organic-inorganic membranes integrating ceramic stiffening additives, [256] such as silica powder, [264] are mainly used in battery integrating the energetically attractive metallic Li electrode to limit the risk of dendrite formation [265] caused by not uniform Li–plating.

The development of the polymer electrolyte continues to hold industrial interest and some compromise approaches have been adopted while breakthrough in solvent free membranes must be achieved. These membranes should transport mainly cations and are solvent free. Attempts, mainly directed toward immobilization of anion in the polymer structure has been reported, but with modest success, as this approach generally depresses the ionic conductivity. So far, the best compromise involves the use of solid–liquid hybrids formed by trapping typical liquid lithium ion solutions (e.g. $LiPF_6$-carbonate solvent mixtures), in a polymer matrix, e.g. poly(acrylo nitrile), PAN or poly(vinylidene fluoride), PVdF, to form gel–type polymer electrolytes, PGEs. The PVDF–HFP based membrane, developed at Bellcore, paved the way for the evolution of these polymer membranes [266, 267]. Ceramic fillers such as SiO_2, Al_2O_3, TiO_2 and $BaTiO_3$ have also been incorporated along with the host polymer in order to obtain composite polymer electrolytes with improved electrical and mechanical properties. [256, 268 269-271] The ceramic fillers promote electrochemical properties, but only by physical action without directly contributing to the lithium ion transport process. By suitable surface modification of the ceramic particles, they can also act as the source of charge carriers. [272-274] An interesting approach, which leads to an enhancement of the transport properties of polymer gel electrolyte is based on the dispersion of core–shell $SiO_2(Li^+)$ particle. This design promotes enhancement of the lithium-ion transference number (0.35 versus 0.48) , associated with the electrolyte uptake.[275]

Another, emerging class of electrolytes is that based on ionic liquids ILs, namely, low temperature molten salts having important specific properties. Typically, ILs are formed by the combination of a weakly interacting, large cation, e.g. of the imidazole type and a flexible anion, e.g. N,N-bis(trifluoromethanesulfonyl), imide (TFSI) [276]. ILs are non-volatile, non-flammable, highly conductive, environmentally compatible and can safely operate in a wide temperature range. This unique combination of favorable properties makes ILs very appealing materials as stable and safe electrolyte media in lithium batteries [276]. But, these solutions have a poor cathodic stability limit associated with the tendency of imidazolium-based cations to be reduced around 1.5V vs. Li. This apparently prevents the use of IL-based solutions with common low voltage anode materials, such as lithium metal, graphite or even $Li_4Ti_5O_{12}$. Many studies are underway to circumvent this issue by developing ILs based on cations more resistant to reduction than those of the imidazolium family.

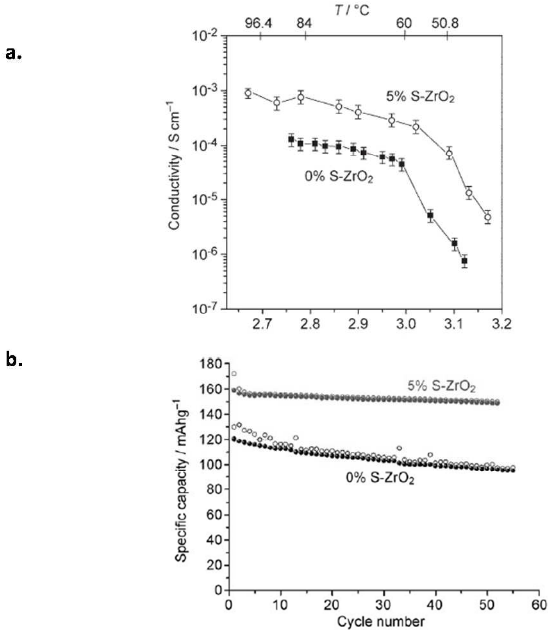


Fig. 6 a. Conductivity Arrhenius plots of composite s-ZrO_2-added electrolyte and of a S-ZrO_2-free electrolyte, both based on the same PEO8LiBF4 combination. Ref [257], b. Capacity versus charge-discharge cycles for the Li/$P(EO)_{20}LiClO_4$ + 5% S-ZrO_2/$LiFePO_4$ battery (upper curve) and the Li/$P(EO)_{20}LiClO_4$/$LiFePO_4$ battery (lower curve). Temperature 90°C; Rate : C/7. The capacity values refer to the cathode. [277]

In fuel cells, Nafion is most common used electrolyte because of its good conductivity, good chemical stability and safety.[278] However, there are also problems associated with these materials. Their conductivity are low at temperature above 120°C and low humidity condition, which narrows the range of practical application for the polymer electrolyte membrane fuel cell (PEMFC). Conductivity in Nafion is due mainly to motion of hydrated proton and may result in large ohmic drop when devices work at high temperature and low humidity limiting the power of the fuel cell. [279, 280] Accordingly, many attempts have been made to overcome these drawbacks. An interesting approach, which leads to enhancement of the transport properties of Nafion is based on the dispersion of nanoparticle fillers, such as SiO_2, TiO_2, SnO_2 within the polymer matric. It has been demonstrated that one of the roles of the filler is that of aiding to retain water into the hydrophilic part of Nafion. [255, 281-286] This water retention maintain water around sulfonic group and then to an increase in the useful range of electrolyte conductivity. Furthermore, the ceramic filler promotes enhancement of the number of mole of water around the sulfonic groups, associated with the Lewis-base interactions occurring between the –OH groups present at the surface of the ceramic filler and the water.

With a few exceptions, these effects have been confirmed by many laboratories. The degree of enhancement depends on the choice of the ceramic filler, the particle size, their morphology and, in particular, of the nature of its surface states. This has been demonstrated by results obtained on a sufonate–promoted superacid SiO_2 ceramic filler. [287-289] The treated SiO_2 has a strong acid strength, associated with the presence of phenyl group between the sulfonate group and the carbonyl chain attached to the surface of the SiO_2. This phenyl group has a high electron–accepting ability, the latter being enhanced by the proximity of the charge withdrawing sulfate groups. Thus at the surface of the oxide, a high density of sulfonate acidic sites are present.

Owing to its high acidity, this modified–SiO_2 ceramic material proved an ideal candidate to test the model. Indeed, its dispersion in the state of the art, Nafion, has led to nanocomposite membrane having unique properties.

Another approach to design hybrid organic–inorganic membranes is to exploit the polar/nonpolar nanophase–separated morphologies of Nafion perfluorinated ionomer membranes, as interactive templates to direct the hydrolysis/condensation reactions of inorganic alkoxides and organoalkoxysilanes.[290-294] Contrasting with pre-formed particles, these polar domains serve as ‘‘nanoreactors’’, and give rise to an inorganic oxide network well–distributed in the hydrophobic organic network. Because in situ polymerisation occurs, this approach allows a better dispersion of the inorganic network in the polymeric matrix compared to the dispersion of pre–formed nanoparticles. The inorganic nanoparticles produced via the sol–gel route are homogeneously distributed on an Angstrom scale versus sub–micrometer length scales for the particle composites. Most often, these hybrids are tailored on a nanoscopic scale. This means that two or more phases have at least one dimension that is less than 100 nm, although length scales ~ 100 A˚ are encountered in some cases.

It is important to point out that the development of polymer electrolytes that conduct only protons and are solvent free is considered of prime importance in order to progress fuel cells. [295-299]

Attempts, mainly directed to avoid Nafion, have been reported in the past, with some success, as this approach generally mimic the phase separation in Nafion, where discrete hydrophobic and hydrophilic regions are present. In this hybrid organic–inorganic design, the hydrophilic regions contain the ionic groups and are supported by the functionalised, mesostructured silica network, while the hydrophobic regions contain the fluorocarbon backbone of the polymer. The most-difficult issue in these hybrid organic–inorganic membranes is to provide the conditions necessary for an efficient proton transfer; that is to say, the formation of percolating, hydrogen-bonded networks in low–humidity conditions, or percolating networks of water filled channels in wet conditions. The properties of these multi–scale membranes are very complex and depend on their structural features and composition, as well as on their inherent dynamic properties. These characteristics can be tuned through the processing approach and various technologies have been used to fabricate hybrid organic–inorganic. In the various processing approaches, solvent evaporation differences directly influence that does directly influence the repartition of the different components. More specifically, the phase separation between the hydrophilic and the hydrophobic domains can be tuned through this evaporation giving rise to hybrid membranes with various microstructures exhibiting different transport properties. Maneeratana *et al.* have shown that hybrid functionalised SiO_2–PVDF membrane synthesised by electrospinning approach exhibit a peculiar and different microstructure and then an enhancement of the proton transport compared to membrane fabricated by casting. The electrospun membrane has high proton conductivity at 120°C and low humidity in addition to improve mechanical properties (figure 7). [300] More importantly, the proton conductivity of these membranes is about 0.1 S/cm at 80°C under 100% of humidity.

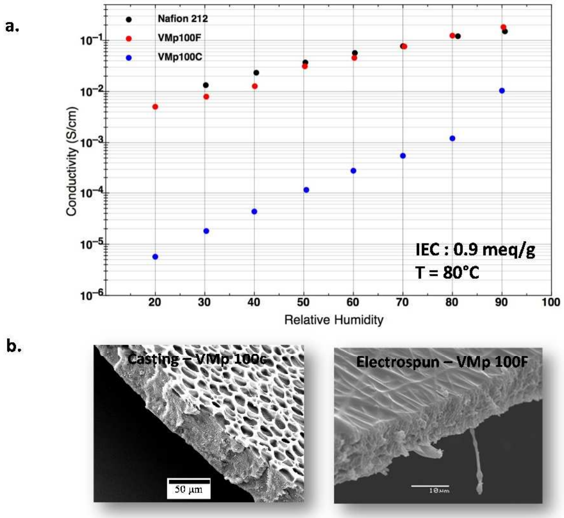


Fig. 7 a) Conductivity of hybrid membrane synthesized by electrospinning and casting approaches. b) Comparison of the microstructure of the electrospun and casted hybrid membrane. [300]

Hybrid organic-inorganic approach for electrode in electrochemical device. So far, hybrid organic–inorganic strategy has been also developed for electrode in Li–ion battery to stabilize the SEI (solid electrolyte interface) at the surface of carbon [301], to maintain contact between silicon particles and graphites flakes [302] or carbon nanotubes [303], and to increase cycle life by limiting electrolyte decomposition at the surface of positive active material. An interesting approach consists of modifying the surface of carbon by covalently attachment of mono- or multi-aryl layers to their surface via diazonium chemistry. [304-306] The aromatic layer forms a stable and uniform solid electrolyte interface that improves the electrochemical behaviour of graphite. [307] This enhancement is demonstrated in figure 8 which compares the specific capacity for original graphite electrode and the modified graphite anode. Clearly, the modified graphite anode keeps at least 98% of its initial capacity after 30 cycles.

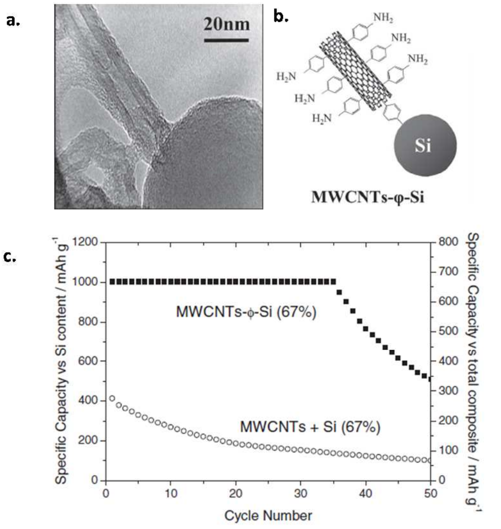


Fig. 8 a) HR–TEM observations of silicon/carbon nanotube composite (MWCNTs–ϕ–Si), b) the corresponding scheme and c) specific capacity vs. cycle number when cycled at a constant current of 500 mA.g^{-1}. [303]

In the electrochemical capacitors field, molecular functionalisation of carbon has been used to provide a novel type of electrical double layer and to increase energy densities. Surface modification with electroactive molecules such as anthraquinone increases the performance of carbon electrodes by adding a faradaic contribution to the double layer capacitance [305, 307]. The modification is also carried out by using diazonium cations electrochemical reduction method developed by Pinson and coworkers [308, 309]. This method involves the formation of aryl radicals, which subsequently react with the carbon surface by forming grafted layers. The addition of redox species to the surface of the carbon with a formal potential close to either the cathodic limit of the carbon or to the anodic limit one provided extra energy and power (figure 9 b). The use of these modified carbon electrodes (anode during discharge) in a carbon supercapacitor has been shown to provide a 40% enhancement in average in capacitance and 5—86% increase in energy density [305]. Martin et al. have also shown that the grafting of aminophenyl groups on graphite–flake surface followed by subsequent grafting of silicon nanoparticle via the diazotization of the second amine group. At the end, the bonding of silicon and graphite by a phenyl molecular bridge has been achieved. [303] Such a covalent linkage is efficient in retaining capacity galvanostatic cycling of the composite material in a lithium cell, with 52% capacity retention after 50 cycles as compared to 38% for a simple mixture of silicon nanoparticles and graphites flakes even when drastic cycling conditions are used.

Hybrid organic-inorganic approach based on metal-organic framework (MOF) has been successfully used in the field of electrode materials for Li-ion battery.[306, 310-312] This solid combines inorganic metal clusters or coordination centres with organic linkers to yield a diversity of three-dimensional structures with porosities. Their properties are highly dependent on their chemical composition and can be tuned either by tuning the mixed valence metallic centres or the redox of the organic linkers. Insertion of redox active species into the pores of Fe^{3+}-MOFs has been studied to determine whether they represent possible positive electrode materials in lithium cells and whether it is possible to take advantage of the large pores in the structure as empty spaces to host lithium cations. [306] The electrochemical reactivity is due to the reduction of Fe^{3+} to Fe^{2+} along with the simultaneous insertion of Li^+ in the structure. Up to 0.6 lithium cation per iron Fe^{3+} is inserted into the MIL-53(Fe) structure at a C/40 rate without any structural alteration to the framework. Despite these good properties, neither the volumetric (mA h cm^{-3}) nor the gravimetric (mA h g^{-1}) electrochemical capacities were very high, because of both the low density of the material and the limited number of inserted Li^+. Limited cyclability at high energy density is due to the poor electronic conductivity of the structure. This poor electronic conductivity was rationalized in terms of interactions between Fe^{3+} and Fe^{2+} sites, which do not allow any electronic delocalization.[313] To push back these two limits, an increase in capacity was achieved through the adsorption of an electro-active molecule, i.e., 1,4-benzoquinone. These molecules can theoretically accept two electrons per molecule and can also play a role as a redox mediator enhancing the electronic transfer in the MIL-53(Fe) structure. Unfortunately, the enhancement of the electrochemical performances, due to the redox properties of the quinone molecules, was observed during the first 2 cycles. An exchange between both the quinone and the electrolyte molecules is proposed to account for the capacity decay in subsequent cycles. More recently, Demir-Cakan et al. used mesoporous chromium trimesate metal organic framework (MOF) named MIL-100(Cr) as host material for sulfur impregnation in Li-S batteries (figure 9). [312]

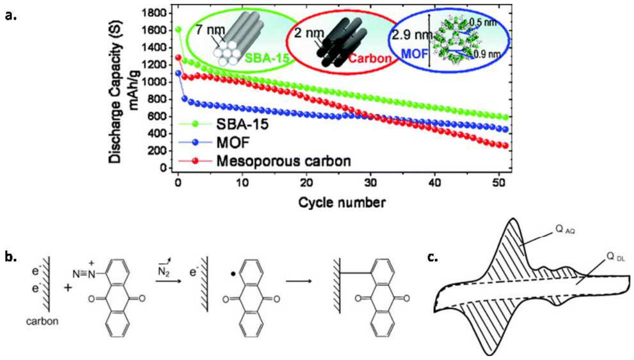


Fig. 9 a) Cycling performance of the composites in 1 M of LiTFSI in TMS electrolyte with C/10 current density for the voltage range between 1.0 and 3.0 V vs Li. for mesoporous SBA-15, Carbon and MOF, [312] b) Chemical modification of carbon by spontaneous reduction of the anthraquinone diazonium cations. c) Representative cyclic voltammogram for an AQ-modified carbon giving the double layer voltammetric charge (Q_{DL}) as well as the voltammetric charge associated to the AQ-grafted groups (Q_{AQ}). [307]

They reported a marked increase in the capacity retention, of Li-S cathodes. Complementary analyses demonstrated the reversible capture and release of the polysulfides by the pores of MOF during cycling and evidenced a weak binding between the polysulphides and the oxygenated framework.

Hybrid organic-inorganic design has been also explored in the development of new photo-electrochemical cell in which light-driven water oxidation to oxygen occurs at the photoanode and reduction of water to hydrogen at the cathode. [314-318]. In this field, the design of hybrid organic-inorganic electrode is often derived from natural photosynthesis. In general, development of water splitting electrochemical devices occurs through the development of the two half reactions, through the combination of a photosensitized with a suitable catalyst for either the oxidation or the reduction of water. To design efficient electrodes, this implies the parallel development of i) efficient and stable electrocatalysts, based on noble and non-noble metals, for accelerating the multi-electronic processes at work at each electrode, ii) efficient and stable photosensitizers for absorbing visible light and generating a charge separation state with redox potentials compatible with water splitting. Different designs have been proposed for synthesizing efficient electrodes based on hybrid approach. The electrocatalyst such as cobaloxime and the photosensitizer were grafted via phosphonated group onto TiO_2 nanoparticle with the aim of taking advantage of the ultrafast electron injection from the excited state of the photosensitized into the conduction band of TiO_2 from which e- can be further transferred to the catalyst (figure 10 a). [315, 316] H_2 is evolved when the system is place at pH = 7 in TEOA aqueous buffer and irradiated with visible light. However, this strategy will suffer from the photo-instability dye. [317, 319]. Alternatively, the co-grafting of an iron-based catalyst has also been demonstrated with evidence for light-driven electron transfer from the excited dye to the catalyst. [318]

Another approach consists of the use of a core-shell nanostructured photoanode (Core : a high surface area conductive metal oxide film indium tin oxide or antimony tin oxide–coated, shell: TiO_2 formed by atomic layer deposition) where a “chromophore-catalyst assembly” 1,[(PO_3H_2)(2)bpy)(2)Ru(4-Mebpy-4-bimpy)Rub(tpy)(OH_2)]($^{4+}$), which combines both light absorber and water oxidation catalyst in a single molecule is grafted onto the surface via phosphonate group. Visible photolysis of the resulting core-shell assembly structure (figure 10 b) with a Pt cathode resulted in water splitting into hydrogen and oxygen with an absorbed photon conversion efficiency of 4.4 at peak photocurrent.

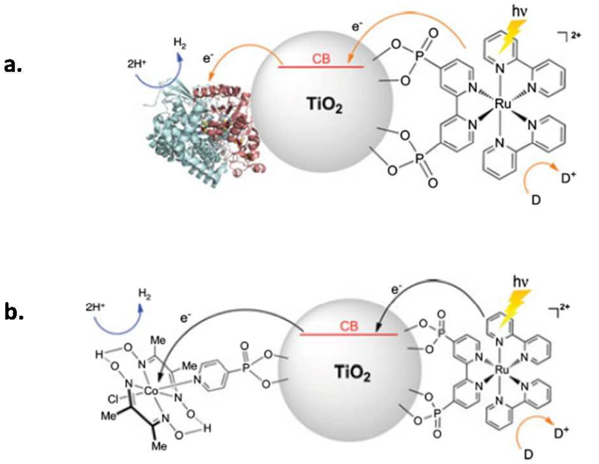


Fig. 10 a) Structure of the TiO_2-based material for H_2 photoproduction using immobilized hydrogenase as catalyst. b) Structure of the TiO_2-based material for H_2 photoproduction using a surface–immobilized cobaloxime catalyst [315], [316]

Commercial applications of hybrid materials

Commercial applications of hybrid materials should not be considered only from a purely scientific point of view. The commercial development of hybrid materials could be achieved if a number of general economic, technical, practical and regulation requirements are fulfilled. As stated previously, observation of the general functioning of industrial world and Nature reveals that both of them are subject to the same general rules and new approaches to be developed imply the same kind of compromise: cost *versus* efficiency. If we consider systems developed by Nature, they involve the use of raw materials easily available in a given environment, leading to complex, robust and multifunctional architectures through smart and particularly well-suited "manufacturing" processes. Besides, they are characterised by an acceptable level of disorder (see chapter entitled "Interfaces with soft matter - Bioinspired surfaces"), a high level of integration into a given ecosystem and a high adaptability to their environment and are most of the time highly competitive. At the same time, commercially developed hybrid materials are elaborated from quite inexpensive precursors greatly available at the industrial scale. Furthermore, the way of hybrid materials processing is highly compatible with proven industrial processing, and final materials have an added value compared to previous materials. Finally, they fulfil safety and regulation requirements. In other words, hybrid materials are integrated in an overall process and their economic viability depends on outside and internal factors. Outside factors include generally availability and cost of chemical precursors, law of supply and demand, competition with other strategies and materials, regulatory constraints such as REACH and RoHS directive. In a near future these factors could favour the development of new approaches by banning the current ones. For example, approaches involving bisphenol A-based materials, chromates and Ni-based phosphate conversion coatings will be avoided. Internal factors imply knowledge of the chemistry involved in the elaboration of new materials, capacity to process new materials with efficient, proven and inexpensive processing, compliance with technical specifications and safety rules, corporate strategy ...).

From a chemical point of view, commercial hybrid materials involves most of the time (bio)polymers or (bio)molecules as organic part, nano-objects (oxides nanoparticles and nanoclays), microcapsules or inorganic molecular precursors as inorganic counterpart and functional organosilanes acting as coupling agents and/or hybrid O-I matrices. [10] The design of hybrid materials clearly follows a bottom-up approach (figure 11). Starting from molecular precursors or well-defined nanobuilding blocks, the materials are processed directly as particles, fibres, coatings, foams or monoliths. They can additionally be obtained with peculiar micropatterning or with hierarchical structures by coupling colloidal fluids with the physical chemistry of complex fluids, soft matter and top down processing strategies. [10, 45] Among these various shapes, films and coatings are one of the most widespread forms that display hybrid materials on the market. Films and coatings concern mainly hybrid materials based on sol-gel process involving mainly functional organosilanes species and are prepared through the chemical solution deposition route. This could be explained by the easiness and rapidity to add new functionalities to a substrate with a quite low amount of starting materials and with a satisfying reproducibility. Furthermore, liquid-deposition devices which are widespread in industry (dip-, spin-, spray-coaters ...) are less expensive than physical-based deposition methods (atomic layer deposition - ALD, physical vapor deposition - PVD …) and usually entail less stringent processing conditions. Bulky materials (monoliths, membranes ...) are also widely present on the market and imply mainly polymers as organic part. Organic polymers provide to hybrid materials an easy shaping and a better processing ability *via* well-known plastics processing techniques (injection, rotational, blow moulding, thermoforming ...) while the inorganic components increase their mechanical and thermal stability in addition to give new specific functionalities (gas barrier, magnetic, electronic, redox, optical properties ...).[42, 320]

This coupling between chemistry and processing techniques (and eventually templating strategy) allows hybrid materials for entering a variety of markets covering various fields such as environment, energy, housing, health, automotive, optics, electronics ... As a detailed description dealing with applications of hybrid materials is out of scope of this chapter, the readers are referred to more specialised reviews and books.[9, 10, 39-41, 44] In the following part, some applications of hybrid materials already on the market will illustrate the previous remarks.

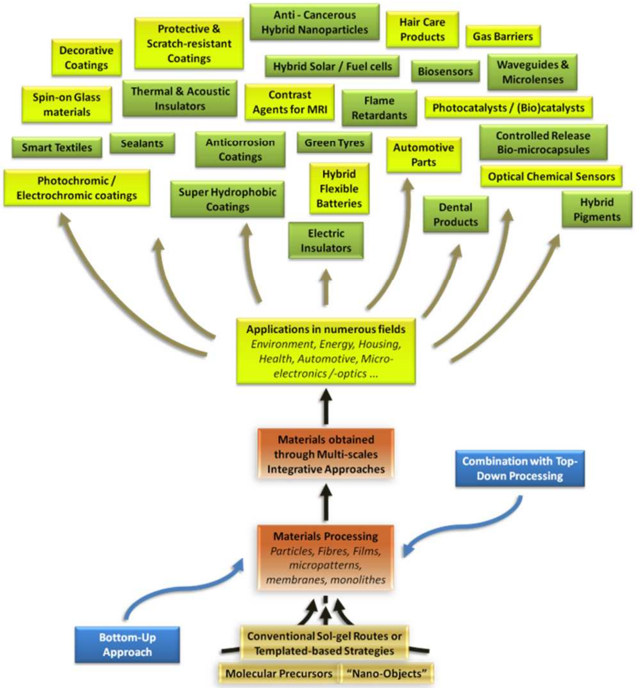


Fig.11 Arborescence representation of hybrid materials on both the academic and industrial scene[10]

Multifunctional hybrid coatings. Optical coatings are probably the most common examples among hybrid coatings applications. As stated previously, the commercial development of (hybrid) materials is partly based on a multifunctional approach, meaning then that coatings often display several additional properties. For example, Schott, pioneer company of sol-gel optical coatings, has developed transparent and easy-to-clean coated glass specifically designed for glass panes of oven baking trays.[321] The SCHOTT® CleanPlus product based on Ormocer is covering glass panes and offers durable hydrophobic properties due to functional hydrophobic siloxanes embedded in an inorganic network layer, withstanding high temperatures and household ustensil abrasion. Another instructive example of optical coatings is provided by coatings on ophthalmic plastic lenses (figure 12). Here again, multifunctionality is required since ophthalmic plastic lenses should present various properties such as transparency, anti-abrasion, anti-smudge, anti-dust combined with the possible variation of transmission with the intensity of light. In this case, multifunctionality is generally achieved through several coatings combined with hybrid chemistry.[322, 323] Concerning anti-scratch property, the coating consists in a compromise: greater surface hardness to limit abrasion caused by fine dust particles and greater flexibility to increase resistance towards larger particles or macroscopic objects. An effective solution has been found by applying a hybrid O-I nano-composite coating to the surface of the lens *via* dip- or spin-coating techniques.[323] These varnishes composed of both organic acrylates based polymers, organosilane coupling agents and mineral nanoparticles (silica for example) solve the problem of abrasion due to their two-fold properties: resistance to fine scratches due to the hardness of their inorganic component and resistance to large scratches due to the flexibility of their organic component. Besides improving the mechanical properties of the coating, the small size of the inorganic nanoparticles eliminates any risk of light scattering and ensures perfect transparency. Moreover, the chemical composition of this first coating provides high adhesion properties on both plastic substrate and subsequent anti-reflective inorganic layers. From a mechanical point of view, this anti-scratch layer ensures a mechanical transition by filling the gap between the mechanical properties of the soft plastic-based lenses and those of the hard anti-reflective mineral layers. Anti-smudge and anti-dust treatments can be additionally performed. The first effect is reached by using in hybrid coatings fluorinated polysilazanes that possess radicals that can react on the silica component yielding good adherence to the coating. Polysilazanes also possess a rich pattern of fluorine that exhibits a strong chemical repulsion to water and oily matter. The second effect requires deposition of anti-static coatings that can be processed by inclusion of transparent conductive components (conductive nanoparticles, ionic species, selected conductive polymers…) to avoid charge accumulation and so the coatings do not attract dust. Moreover these hybrid coatings can be compatibilised with organic dyes as chromens or spyro-oxazines to yield photochromic lenses, whose transmission varies with the intensity of light and thus adapt to diverse lighting conditions.

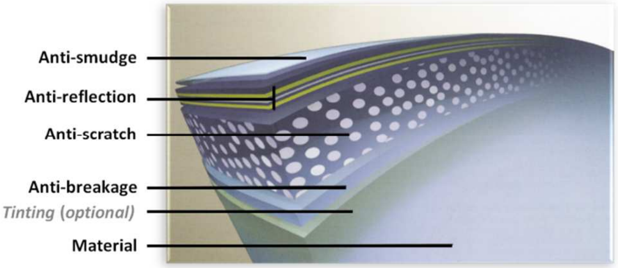


Fig. 12 Structure of an ophthalmic lens. (Courtesy of Essilor International)

The last example concerns commercialised hybrid protective coatings such as conversion layers. Conversion layers have been developed in the last decade in both aeronautics and automotive domains (*for aeronautics: AC-130/AC-131 products of 3M Aerospace Sealants, Socogel B0102/B0202 sold by Socomore,* *DesoGel products of PPG Aerospace and for automotive: Zircobond® products provided by PPG industries, Oxsilan® products of Chemetall ...*). The development of these new conversion layers is mainly due to a tightening of legal regulations which aims to ban highly toxic chromates- and nickel-based conversion layers. Besides compliance with regulations, such coatings should also fulfil several technical and economical requirements. They should present a satisfying adhesion to metallic alloys enhancing thus passive corrosion resistance and should favour high adhesion ability to the organic-based resins constituting primers and/or topcoats. In addition to that, the composition of conversion layers should be adapted to accommodate thermal expansion of both metallic substrates and top-layers, minimising thus the formation of cracks as far as possible over a wide range of temperatures. Such water-based products are typically made of organozirconium and organosilane mixture. The Zr-based precursor bonds covalently with the metal surface (Zr-O bond is stronger than Ti-O or Si-O bonds) while the organosilane coupling agent holding a reactive functional group preferentially grafts with the adhesive or matrix resin subsequently deposited. The organic moiety of siloxane precursor is favorably chosen regarding the resin type, for example glycidoxy-alkylsilane for epoxy or urethane matrixes and primary amine such as amino-alkylsilane for polyimide-based resins. Another advantage of hybrid conversion layers concerns the versatility of the deposition step. Indeed, coating and curing processes of hybrid conversion layers are highly compatible with existing automotive pretreatment and coating lines, limiting thus the extra-cost of this new technology. Moreover, these new hybrid coatings can be deposited by spraying instead of dipping, which is more adapted to the coating of large aircrafts components and which allows for reducing solution amounts and wastes.

Hybrid (nano)particles for body care and pharmaceutical applications. The area of research concerning nanopharmacy / nanomedicine has really exploded during the past decade. The surge of smart hybrid nanomaterials has yielded a few products that have entered in the real market. [324, 325] Indeed, hybridized inorganic nanoparticles are found in applications as active pharmaceutical ingredient, as vectors or with an enabling function. Some others are used for in vitro diagnosis as in lateral flow devices (immunochromatographie) or in delivery systems (drug delivery, as implantable biomaterials, vaccine adjuvants). Many new hybrids are already developed as prototypes or in early preclinical trials fitting the reality of production and regulatory difficulties inherent to the entry of any new commercial product into, in particular, markets associated to human health and medicine. [324]

For example, Sol-Gel Technologies company has developed a set of *class I* hybrids compounds which some of them are sold by Merck KgaA *(Eusolex® UV-Pearls™)* and EMD Chemicals Inc (figure 13). [326] These new hybrid compounds target the field of cosmetics and controlled release of "active ingredients" and, in particular, for applications concerning skin care and protection. [327, 328] Undesirable skin alterations and melanomas created by sun induced premature skin aging need the use of efficient but biocompatible sunscreens. Hybrids developed by Sol-Gel Technologies are based on the encapsulation of active organic components within nanoporous silica micro-capsules. They present several advantages compared to current commercial sunscreens. Indeed, by encapsulating the active organic UV filters (80% w/w of the final product) in silica micro-capsules, the contact of these chemicals with the skin is reduced, and damage from free radicals that may get trapped within the porous host preventing radical damage to the DNA. In particular, these "UV-pearls" incorporated into a suitable cosmetic vehicle to achieve high Sun Protection Factors (SPF), while affording an improved safety profile as the penetration of the UV absorbers is markedly reduced, have already been adopted by companies for sunscreens and daily wear cosmetics. [326] The same company has also developed silica rainbow pearls containing organic dyes for cosmetics applications and silica active-pearls ("cool pearls") containing an effective acne medicament as benzoyl peroxide, which are as effective as antibiotics but does not causes bacterial resistance or stomach upset. Benzoyl peroxide, in direct contact with skin, provokes skin irritations, dryness and hyper-pigmentation in many patients. Sol-gel active-pearls have undergone successful commercial development because embedding the benzoyl peroxide active ingredient in a silica shell prevents it from coming into contact with epidermis while gradually delivering it to follicular region where acne bacteria are located.

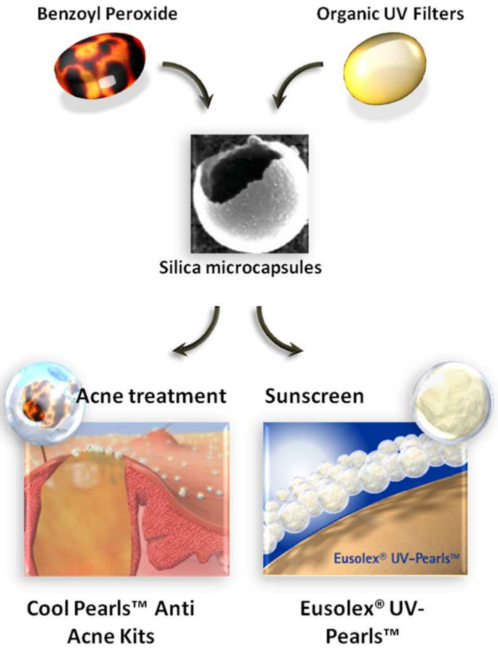


Fig. 13 Encapsulation of drugs / organic UV filtres in protective silica micropearls for acne treatment and sunscreens (courtesy of Sol-Gel Technologies and Merck Chemicals respectively)

Another approach based on the physical intrinsic properties of the inorganic part of hybrid materials involves hybridized inorganic nanoparticles (NPs) such as (ultrasmall) superparamagnetic iron oxide NPs (SPIO/USPIO), gold-based core-shell NPs (silica core of about 100 nm and a gold shell of 20 nm - AuroShell®), crystallised hafnium oxide-based NPs (NanoXray®) or gold-based NPs (TobacAlert™) ... [10, 325] Briefly, magnetic iron oxide particles formulations (SPIO, USPIO) are used for in vivo imaging through Magnetic Resonance Imaging

(MRI) and for thermal cancer therapy via hyperthermia. Gold shell NPs yield photothermal cancer therapy nanodevices that operate using thermal ablation; the heat associated to their characteristic plasmonic response (AuroShell®). Both, hyperthermia and thermal ablation are therapies related to the use of heat as a way of action to kill pathophysiological tissues. Another possibility concerns the use of locally generated reactive radicals through X-ray excited inorganic nano-absorbers to destroy the tumour (NanoXray®).

Hybrid aerogels and polymer nanocomposites. Unsuccessfully commercialised in the 1940's - 90's by several companies (Monsanto, BASF ...), silica-based aerogels have been re-commercialised in the 2000's. This was achieved thanks to the research developed in the 1980's - 90's and focused on both chemistry and processing of aerogels. These developments allowed fabrication of aerogels more compatible with industrial and commercial requirements. Aerogel manufacturing at larger scale has become safer, faster and less expensive thanks to the development of both supercritical drying with technically less constraining and non-flammable supercritical CO_2 fluid and the ambient-pressure drying which is based on series of solvent-exchange processes and chemical surface modification with an hydrophobic organosilane. [329-331] It is interesting to notice that the supercritical drying has been selected by Aspen Aerogels® for producing composites materials while the ambient-pressure drying is currently used by several companies for producing translucent hydrophobic silica-based aerogels granules (for example Cabot Corporation under the tradename Nanogel™ or Dow Corning under the product name VM 2270 Aerogel Fine Particles - figure 14). [10]

Fig. 14 Some commercial products based on hybrid O-I aerogel. *Aerogel Products:* Various hybrid aerogel products commercially available (top: Aspen Aerogel® flexible composite blankets / down: Nanogel™ translucent granules and fine particles - Cabot Corporation®)

Despite the amazing intrinsic characteristics and properties of aerogels, most as-made aerogels present a poor mechanical behaviour: they are often highly brittle and fragile. This represents a serious drawback for their commercial applications. O-I hybridization of aerogels overcomes this lack of mechanical properties. Several strategies have been developed resulting in an increase of mechanical properties and facilitating then their further handling. One of these strategies is based on the co-condensation of a flexible polydimethylsiloxane (PDMS) with TEOS [332] or involves methyltrimethoxysilane as unique precursor. [333, 334] Gels obtained present a rubber-like flexibility and display high compression capability. In addition to the improvement of mechanical properties, these aerogels are highly hydrophobic (contact angle > 160°) and could absorb 10-20 times their own weight in (toxic) apolar liquids (petrol, kerosene and diesel for example). Interestingly, this last property *i.e.* oil absorption capability allowed Dow Corning company and Cabot Corporation to commercialise methylsilylated aerogel as fragrance delivery and retention materials, thickener, sebum absorber and soft focus agent for personal care and as oil spill management respectively.

Another interesting way enhancing the mechanical properties of aerogels consists in the doping/reinforcing of aerogels by crosslinking organic polymers on the original gel skeletons. Based on the observation that polymers could be reinforced by inorganic fillers, Leventis *et al.* successfully increase the mechanical properties of aerogels by doping fillers (*i.e.* aerogels) with polymers. [335-337] However if the mechanical properties (strength, stiffness, flexibility …) are usually enhanced by the organic polymerisation, the insulating ability, optical transparency, surface area are in the same time reduced.

The last way increasing the mechanical properties of aerogels and leading to a commercial development is based on another type of reinforcement. Like steel bars reinforce concrete in buildings, aerogels could be reinforced by microfibers. Using this approach, Aspen Aerogels started to fabricate in the early 2000's flexible fiber-hydrophobic silica aerogel composite blankets *via* a sol impregnation process followed by supercritical drying with CO_2. Depending on the formulation of composites (for example the type of fibers organic or inorganic), aerogel-based insulation blankets were designed for cryogenic applications (Cryogel®), for clothing and apparel (Pyrogel® / Spaceloft®) or for high-temperature applications (Pyrogel®) allowing then insulation from - 265°C to 650°C. Moreover, due to their low thickness, flexibility and easy handling features, they could easily insulate any type of plant's equipment (piping, towers, tanks …) even in confined spaces. Their products are now found in subsea oil pipelines (pipe in pipe insulation), refineries, winter apparel, building and construction.

Considering now the high optical transparency of aerogels in addition to their insulation properties (thermal and acoustic), Cabot Corporation incorporated its Nanogel® granules in daylighting systems providing an enhancement of insulation while maintaining optimal light transmission. Aerogel granules / particles could be incorporated in many existing daylighting systems (structural composite panels, structural polycarbonate systems, U-channel glass, insulated glass units ...).

Another important development leading to commercial products concerns hybrid polymers nanocomposites (PNCs). Basically, PNCs could be described as the combination of a polymer matrix with inorganic or hybrid nano-objects that have at least one dimension in the nanometer range (length scale below 100 nm). Considering the extensive variety of both nano-objects (oxide-based particles, oxo-clusters, POSS, clays, nanoMOFs, metals, quantum dots, carbon nanotubes, …) and existing polymers, their potential combinations and thus the synergetic properties of the resulting PNCs are essentially endless. Generally, PNCs imply low-volume additions (1-10%) of nano-objects which provide mechanical properties (like elastic stiffness and strength) enhancements with respect to the neat polymer that are comparable to that achieved by conventional loadings (15-40%) of traditional micrometer-scale inorganic fillers. This is generally explained by the large surface area to volume ratio of nano-objects when compared to the micro- and macro-additives. In addition to that, the lower particles loading facilitates processing and reduces component weight. Most important are the unique value-added properties and property combinations, normally not possible with traditional fillers, such as barrier resistance, optical clarity, scratch/wear resistance, flame retardancy, oxidation, and ablation resistance. This incredible versatility in terms of chemistry combined with easy and existing processing could easily explain the abundance of articles, patents and finally commercial products related to PNCs over the past 20 years.

Commercial developments of PNCs involve mainly two types of nano-objects: oxide-based particles (silica-based particles most of the time) and clays due to their commercial availability and their relatively low cost. Although several strategies have been investigated to prepare PNCs depending on the starting states of both organic and inorganic materials, [170, 173-175, 178, 338-344] in practice, the majority of commercial developments involves preformed nano-objects. These nano-objects could be incorporated in the polymer matrix by (i) melt processing (direct mixing of nano-objects with the polymer melt), by (ii) solution processing (a common solvent is used to disperse nano-objects in a polymer solution), by (iii) an *in-situ* polymerisation (dispersion of nano-objects directly in the monomer or monomer solution). From a chemical point of view, these inorganic nano-objects (clays and oxide-based particles) usually present a hydrophilic characteristic which could seriously impede homogeneous dispersion in the organic polymer phase leading then to materials presenting properties similar to traditional micro-composites. Functionalisation of these nano-objects requires molecules able to both bond to the particles surface and to interact with the polymer matrix. They should then present anchoring groups interacting with the inorganic particles through covalent, coordinative, electrostatic or hydrogen bonding and an organic part capable of forming covalent bonds (through a polymerisation process) to the polymer matrix or interacting *via* van der Waals forces. [170, 173-175, 178, 338-347]

The example concerning "green tyres" is of particular interest since its impact on our environment and on the industrial producing is significant. The wear resistance of filled rubber is essentially determined by the filler characteristics, especially surface activity and morphology. High surface area carbon black, giving large interfacial area between filler and polymer combined with its high affinity towards rubber (through van der Waals forces), induces high interaction with the hydrocarbon polymer used in tyres, resulting in improved wear resistance. In the beginning of 1990's, a collaboration between Michelin and Rhodia allowed the incorporation of "highly dispersive silica" (HDS) nanoparticles into tyre tread. In order to minimise filler-filler interactions, while at the same time for favouring polymer-filler interactions, a surface-modification of the nanoparticles was necessary. It was achieved by their functionalisation with a coupling agent, bis(3-triethoxysilylpropyl-) tetrasulfane (TESPT) which allows covalent bonding between organically-modified nanoparticles and SBR (styrene-butadiene rubber) polymer chains during the vulcanization process. [348] This functionalisation was essential since bare silica nanoparticles show a very low polymer-filler interactions leading to a strong tendency to agglomerate. In term of processing, this innovation implied the adaptation of tyre manufacturing and specially the mixing step. In the case of black carbon, the mix consists of essentially decreasing the size of aggregates (around 80 nm). In contrast, silica nanoparticles added in mixers before organically-modification and particles functionalisation takes place in mixers. A careful control of both temperature and mixing time is needed to first organically modify nanoparticles and next to covalently bond these modified nanofillers to the polymers during the vulcanization process. [348] This example of nanofillers in tyres manufacturing, carbon black versus silica nanoparticles, is not only related to their reinforcing ability *i.e.* improvement of mechanical properties of the final nanocomposites. It emphasises also the importance of additional intrinsic properties of nanofillers. In contrast to HDS nanoparticles, carbon black presents anti-UV properties and a deep black colour which masks the coloured oxidised forms of anti-oxidative agents present in tyre composition. [349] These additional properties combined with its lower costs explain the essential part of carbon black as nanofillers.

Another well-known commercial application of PNCs related to automotive industry was developed by researchers of Toyota in the early 1990's and concerns clays-based PNCs. [174, 350-353] Since this pioneering work, research and commercial developments about clays-based PNCs have exploded during the past 20 years. However, preparations of clays-based PNCs are not straightforward. Indeed, the layered structure of clays deeply influences the final properties of PNCs. Depending on the compatibility between organic polymers and clays, clays could display an intercalated or exfoliated structure into the PNCs. From an industrial point of view, three main properties of clays-based PNCs have been commercially exploited: improvement of mechanical properties of polymers, gas barriers performance, and fire / heat resistance. Thus markets concerned by clays-based PNCs are mainly automotive and food / beverage packaging.

The first commercial application of these materials was the use of clay/nylon-6 nanocomposites as timing belt covers for Toyota cars (the "Starlet" passenger car), in collaboration with Ube Ind. in 1989. [174] Shortly after this first commercialisation, Unitika Ltd. introduced nylon-6 nanocomposites for engine covers on Mitsubishi's gasoline direct injection (GDI) engines. [354] However for cost reasons, these early applications were unable to retain their position in the highly competitive automotive markets. It was not until the 2000s that new clay-based materials re-entered in the automotive industry (PP and TPO-based PNCs). In the 2002, General Motors, in cooperation with Basell North America and Southern Clay Products, developed an exterior step assist component for its GMC Safari and Chevrolet Astro models. This component was made with a PP-based nanocomposite containing 2.5% of nano-clay in place of 15% talc. The PNC presented numerous advantages compared to the talc-based composite: it was lighter in weight, stiffer, more robust at low temperatures and more recyclable. It helped also to reduce paint delamination, and improved knit-line appearance, colourability, grain patterns, scratch and mar resistance. In term of processing, it presented the advantage to be moulded in the same tool that the talc-based composite. However, specific modifications of the moulding tool were performed to avoid clay agglomeration during processing. Engineers optimised several processing parameters such as the clay infeed position at the extruder, the screw design, screw speed, temperature, and pressure. Optimisation of the clay dispersion into the polymer matrix was also achieved by chemical improvements in the nano-clays' surface modification and polymer formulation, leading then to a high rate of exfoliation. Progress in both chemical and processing domains has allowed a development of PNCs use in the automotive field. Interestingly, Pirelli has developed a new tyre involving two PNCs in the tread of high performance tyres series (winter 240 Sottozero for example - figure 15). Briefly, this tyre series utilises cap and base technology that combines two different compounds in the tread. The upper part (cap) of the tread that comes into contact with the road surface uses silica-based PNCs (as previously mentioned with Michelin's tyres) providing greater stability in both wet and dry conditions. The sub-part of tread in contact with the casing (base) uses organically modified nano-clays dispersed throughout the polymer and provides the stiffness that enhances stability and driving precision and an equal performance in longitudinal and lateral directions.

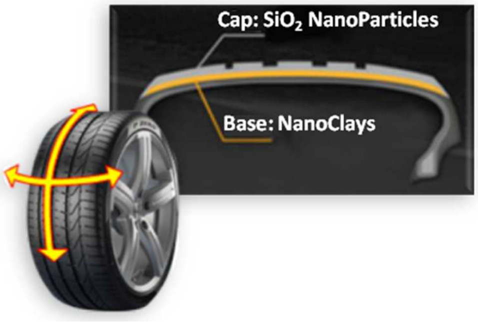


Fig. 15 Pirelli's tyres based on cap (hybrid silica nanoparticles-based PNCs) and base (nanoclay-based PNCs) technology (*courtesy of Pirelli*®)

Besides automotive applications, clay-based PNCs have been also employed in food and beverage packaging as well as for barrier liners in storage tanks and fuel lines due to their excellent barrier properties. These properties are commonly explained by the formation of a labyrinth resulting of the spatial dispersion of nano-clays platelets within the polymeric structure, which physically delays the passage of gas and vapour. Examples of applications concern modified atmosphere packaging for food (meats, cheese, confectionery, cereals and boil-in-the-bag), extrusion-coating applications in association with paperboard for fruit juice and dairy products, and together with co-extrusion processes for the manufacture of beer and carbonated drinks bottles.

Conclusion, Perspective, Future of hybrid materials

Hybrid materials being at the interface of organic (biologic) and inorganic realms are highly versatile offering a wide range of possibilities to elaborate tailor-made materials in terms of processing, chemical and physical properties. Today, a multitude of functional hybrid materials span a very large and diverse set of structures, textures and chemical compositions. In addition they present a high versatility with regard to shaping. As a consequence they are extremely competitive candidates for numerous applications such as those already described in the present article and in several other review articles. [9, 10, 41] The growth and importance of this multidisciplinary scientific domain can be illustrated by a respectable number of international conferences, themed issues published in high impact journals and books, scientific articles (in green) and patents (in orange) (figure 16).

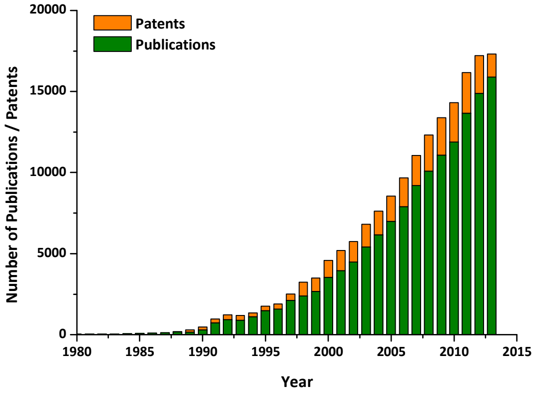


Fig. 16 Number of papers (Isi Web of Knowledge^{SM}) and patents (WIPO) that use the concept of sol-gel derived hybrids, hybrid materials, O-I nanocomposite, bionanocomposite, ormocers, ormosils, coordination polymers and metal organic frameworks.

Futures researches will give birth to more complex bioinspired hybrid materials and systems. These new generation of hybrid materials will combine many interesting features such as miniaturization, hierarchical organizations, resistance, recognition, self-repairing properties and adaptability. Tomorrow, as in living organisms hybrid materials will be integrated in smart devices that will present homeostatic abilities, maintaining tight control of their local environment through interconversions of chemical, electrochemical and mechanical energy and self-regulating feedback loops organized hierarchically across many length scales. [355] Let's have a dream: these innovative hybrid materials will be fully recyclable or they even will be able to self-replicate.

Notes and references

[a] *Sorbonne Universités UPMC Univ Paris 06, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France.*
Fax: +33-144271504; Tel: +33-144271501; E-mail: clement.sanchez@upmc.fr, christel.laberty@upmc.fr, laurence.rozes@upmc.fr, lionel.nicole@upmc.fr
[b] *CNRS, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France.*
Fax: +33-144271504; Tel: +33-144271501; E-mail: clement.sanchez@upmc.fr, christel.laberty@upmc.fr, laurence.rozes@upmc.fr, lionel.nicole@upmc.fr
[c] *Collège de France, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005, Paris, France.*
Fax: +33-144271504; Tel: +33-144271501; E-mail: clement.sanchez@college-de-france.fr, christel.laberty@upmc.fr, laurence.rozes@upmc.fr, lionel.nicole@upmc.fr

1. B. Bhushan, *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences*, 2009, **367**, 1445-1486.
2. P. Fratzl and R. Weinkamer, *Progress in Materials Science*, 2007, **52**, 1263-1334.
3. G. Rytwo, *Macla*, 2008, **9**, 15-17.
4. E. Ruiz-Hitzky, P. Aranda, M. Darder and G. Rytwo, *Journal of Materials Chemistry*, 2010, **20**, 9306-9321.
5. F. Bergaya and G. Lagaly, *Handbook of Clay Science*, Elsevier Science2013.
6. A. Weiss, *Angewandte Chemie-International Edition*, 1963, **2**, 697-703.
7. M. S. Del Rio, P. Martinetto, C. Reyes-Valerio, E. Dooryhee and M. Suarez, *Archaeometry*, 2006, **48**, 115-130.
8. H. Berke, *Chemical Society Reviews*, 2007, **36**, 15-30.
9. C. Sanchez, B. Julian, P. Belleville and M. Popall, *Journal of Materials Chemistry*, 2005, **15**, 3559-3592.
10. C. Sanchez, P. Belleville, M. Popall and L. Nicole, *Chemical Society Reviews*, 2011, **40**, 696-753.
11. J. Livage, *Le Monde*, 1977, October 26th.
12. N. Gharbi, C. Sanchez, J. Livage, J. Lemerle, L. Nejem and J. Lefebvre, *Inorganic Chemistry*, 1982, **21**, 2758-2765.
13. D. Avnir, D. Levy and R. Reisfeld, *Journal of Physical Chemistry*, 1984, **88**, 5956-5959.
14. H. Schmidt, H. Scholze and A. Kaiser, *Journal of Non-Crystalline Solids*, 1984, **63**, 1-11.
15. J. Livage, M. Henry and C. Sanchez, *Progress in Solid State Chemistry*, 1988, **18**, 259-341.
16. C. Sanchez, J. Livage, M. Henry and F. Babonneau, *Journal of Non-Crystalline Solids*, 1988, **100**, 65-76.
17. C. Sanchez and F. Ribot, *Proceedings of the First European Workshop on Hybrid Organic- Inorganic Materials - New Journal of Chemistry*, 1993, **18**, 987-988.
18. C. Sanchez and F. Ribot, *New Journal of Chemistry*, 1994, **18**, 1007-1047.
19. D. Avnir, *Accounts of Chemical Research*, 1995, **28**, 328-334.
20. D. Avnir, V. R. Kaufman and R. Reisfeld, *Journal of Non-Crystalline Solids*, 1985, **74**, 395-406.
21. D. Levy, S. Einhorn and D. Avnir, *Journal of Non-Crystalline Solids*, 1989, **113**, 137-145.
22. F. Gelman, J. Blum and D. Avnir, *Journal of the American Chemical Society*, 2002, **124**, 14460-14463.
23. Y. Aouat, G. Marom, D. Avnir, V. Gelman, G. E. Shter and G. S. Grader, *Journal of Physical Chemistry C*, 2013, **117**, 22325-22330.
24. L. Shapiro and D. Avnir, *Chemcatchem*, 2013, **5**, 2195-2198.
25. R. Zusman, C. Rottman, M. Ottolenghi and D. Avnir, *Journal of Non-Crystalline Solids*, 1990, **122**, 107-109.
26. B. Iosefzon-Kuyavskaya, I. Gigozin, M. Ottolenghi, D. Avnir and O. Lev, *Journal of Non-Crystalline Solids*, 1992, **147-148**, 808-812.
27. C. Rottman, M. Ottolenghi, R. Zusman, O. Lev, M. Smith, G. Gong, M. L. Kagan and D. Avnir, *Materials letters*, 1992, **13**, 293-298.
28. C. Rottman, A. Turniansky and D. Avnir, *Journal of Sol-Gel Science and Technology*, 1998, **13**, 17-25.
29. S. Braun, S. Rappoport, R. Zusman, D. Avnir and M. Ottolenghi, *Materials Letters*, 1990, **10**, 1-5.
30. D. Avnir, T. Coradin, O. Lev and J. Livage, *Journal of Materials Chemistry*, 2006, **16**, 1013-1030.
31. IL 120022; US 6,159,453; EP 0973493; WO/1998/031333, 2000.
32. US 6,238,650; EP 1181001; WO/2000/072806, 2001.
33. IL 141411; US 6,303,149; EP 1104287; WO/2000/009652, 2001.
34. US 6,436,375; EP 1181000; WO/2000/071084, 2002.
35. US 6,468,509, 2002.
36. US 7,758,888, 2010.
37. US 8,039,020, 2011.
38. US 8,449,918, 2013.
39. P. Gómez-Romero and C. Sanchez, eds., *Functional Hybrid Materials*, Wiley-VCH, Weinheim2004.
40. G. Kickelbick, ed., *Hybrid Materials: Strategies, Syntheses, Characterization and Applications*, Wiley-VCH, Weinheim2007.
41. H. Schmidt, *Journal of Sol-Gel Science and Technology*, 2006, **40**, 115-130.
42. F. Mammeri, E. Le Bourhis, L. Rozes and C. Sanchez, *Journal of Materials Chemistry*, 2005, **15**, 3787-3811.
43. M. A. Aegerter and M. Mennig, eds., *Sol-Gel Technologies for Glass Producers and Users*, Kluwer Academic Publishers, Boston / Dordrecht / New York / London, 2004.
44. R. K. Gupta, E. Kennel and K.-J. Kim, eds., *Polymer Nanocomposites Handbook*, CRC Press - Taylor & Francis Group2010.
45. M. Faustini, C. Boissiere, L. Nicole and D. Grosso, *Chemistry of Materials*, 2014, **26**, 709-723.
46. C. Sanchez, ed., *Functional hybrid materials* Journal of Materials Chemistry, **15**, 3543-3556, 2005.
47. J. Long and O. Yaghi, eds., *Metal Organic Frameworks*, Chemical Society Reviews, **38**, 1201-1508, 2009.
48. P. Rabu and A. Taubert, eds., *Advanced Hybrid Materials*, Journal of Materials Chemistry, **20**, 9263-9562, 2010.
49. C. Sanchez, S. Kitagawa and K. Shea, eds., *Hybrid materials* Chemical Society Reviews, **40**, 453-1152, 2011.
50. S. Mann, S. L. Burkett, S. A. Davis, C. E. Fowler, N. H. Mendelson, S. D. Sims, D. Walsh and N. T. Whilton, *Chemistry of Materials*, 1997, **9**, 2300-2310.
51. B.-L. Su, C. Sanchez and X.-Y. Yang, eds., *Hierarchically Structured Porous Materials: From Nanoscience to Catalysis, Separation, Optics, Energy, and Life Science*, Wiley-VCH, Weinheim, 2011.
52. F. Hoffmann, M. Cornelius, J. Morell and M. Froba, *Journal of Nanoscience and Nanotechnology*, 2006, **6**, 265-288.
53. F. Hoffmann and M. Froba, *Chemical Society Reviews*, 2011, **40**, 608-620.
54. D. A. Loy and K. J. Shea, *Chemical Reviews*, 1995, **95**, 1431-1442.
55. K. J. Shea and D. A. Loy, *Chemistry of Materials*, 2001, **13**, 3306-3319.
56. B. Boury and R. J. P. Corriu, *Chemical Communications*, 2002, 795-802.
57. M. Barboiu, A. Cazacu, M. Michau, R. Caraballo, C. Arnal-Herault and A. Pasc-Banu, *Chemical Engineering and Processing*, 2008, **47**, 1044-1052.
58. G. A. Ozin, *Chemical Communications*, 2000, **6**, 419-432.
59. W. D. Wang, J. E. Lofgreen and G. A. Ozin, *Small*, 2010, **6**, 2634-2642.
60. U. Schubert, *Chemical Society Reviews*, 2011, **40**, 575-582.
61. Y. Chujo and T. Saegusa, *Advances in Polymer Science*, 1992, **100**, 11-29.
62. C. Sanchez, G. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer and V. Cabuil, *Chemistry of Materials*, 2001, **13**, 3061-3083.
63. U. Schubert, N. Husing and A. Lorenz, *Chemistry of Materials*, 1995, **7**, 2010-2027.
64. R. J. P. Corriu, *C. R. Acad. Sci. Paris, Série IIC*, 1998, **1**, 83-89.
65. C. Sanchez, C. Boissiere, S. Cassaignon, C. Chaneac, O. Durupthy, M. Faustini, D. Grosso, C. Laberty-Robert, L. Nicole, D. Portehault, F. Ribot, L. Rozes and C. Sassoye, *Chemistry of Materials*, 2014, **26**, 221-238.
66. G. J. A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, *Chemical Reviews*, 2002, **102**, 4093-4138.
67. T. X. Fan, S. K. Chow and D. Zhang, *Progress in Materials Science*, 2009, **54**, 542-659.
68. A. R. Parker, *Journal of Optics a-Pure and Applied Optics*, 2000, **2**, R15-R28.
69. L. P. Biro and J. P. Vigneron, *Laser & Photonics Reviews*, 2011, **5**, 27-51.
70. J. Boulenguez, S. Berthier and F. Leroy, *Applied Physics a-Materials Science & Processing*, 2012, **106**, 1005-1011.
71. A. L. Ingram and A. R. Parker, *Philosophical Transactions of the Royal Society B-Biological Sciences*, 2008, **363**, 2465-2480.

72. S. Berthier, *Photonique des Morphos*, Springer-Verlag, Paris, 2010.
73. S. Kinoshita and S. Yoshioka, *Chemphyschem*, 2005, **6**, 1442-1459.
74. S. Berthier, *Applied Physics a-Materials Science & Processing*, 2005, **80**, 1397-1400.
75. Y. M. Zheng, X. F. Gao and L. Jiang, *Soft Matter*, 2007, **3**, 178-182.
76. G. D. Bixler and B. Bhushan, *Soft Matter*, 2012, **8**, 11271-11284.
77. S. Nishimoto and B. Bhushan, *Rsc Advances*, 2013, **3**, 671-690.
78. T. Saison, C. Peroz, V. Chauveau, S. Berthier, E. Sondergard and H. Arribart, *Bioinspiration & Biomimetics*, 2008, **3**.
79. A. R. Parker and H. E. Townley, *Nature Nanotechnology*, 2007, **2**, 347-353.
80. R. J. Martin-Palma, C. G. Pantano and A. Lakhtakia, *Applied Physics Letters*, 2008, **93**.
81. A. Lakhtakia, R. J. Martin-Palma, M. A. Motyka and C. G. Pantano, *Bioinspiration & Biomimetics*, 2009, **4**.
82. G. Cook, P. L. Timms and C. Goltner-Spickermann, *Angewandte Chemie-International Edition*, 2003, **42**, 557-559.
83. J. Y. Huang, X. D. Wang and Z. L. Wang, *Nano Letters*, 2006, **6**, 2325-2331.
84. D. P. Gaillot, O. Deparis, V. Welch, B. K. Wagner, J. P. Vigneron and C. J. Summers, *Phys. Rev. E*, 2008, **78**, 031922.
85. S. Sotiropoulou, Y. Sierra-Sastre, S. S. Mark and C. A. Batt, *Chemistry of Materials*, 2008, **20**, 821-834.
86. M. R. Jorgensen and M. H. Bartl, *Journal of Materials Chemistry*, 2011, **21**, 10583-10591.
87. D. P. Pulsifer and A. Lakhtakia, *Bioinspiration & Biomimetics*, 2011, **6**, 031001.
88. D. Zhang, *Morphology Genetic Materials Templated from Nature Species*, Zhejiang University Press - Springer Berlin Heidelberg2012.
89. H. Zhou, T. X. Fan and D. Zhang, *Chemsuschem*, 2011, **4**, 1344-1387.
90. K. Yu, T. Fan, S. Lou and D. Zhang, *Progress in Materials Science*, 2013, **58**, 825-873.
91. S. H. Kang, T. Y. Tai and T. H. Fang, *Current Applied Physics*, 2010, **10**, 625-630.
92. J. Silver, R. Withnall, T. G. Ireland and G. R. Fern, *Journal of Modern Optics*, 2005, **52**, 999-1007.
93. J. Silver, R. Withnall, T. G. Ireland, G. R. Fern and S. Zhang, *Nanotechnology*, 2008, **19**.
94. B. Li, J. Zhou, R. L. Zong, M. Fu, Y. Bai, L. T. Li and Q. Li, *Journal of the American Ceramic Society*, 2006, **89**, 2298-2300.
95. C. Mille, E. C. Tyrode and R. W. Corkery, *Chemical Communications*, 2011, **47**, 9873-9875.
96. C. Mille, E. C. Tyrode and R. W. Corkery, *RSC Advances*, 2013, **3**, 3109-3117.
97. J. P. Vernon, Y. N. Fang, Y. Cai and K. H. Sandhage, *Angewandte Chemie-International Edition*, 2010, **49**, 7765-7768.
98. J. P. Vernon, N. Hobbs, Y. Cai, A. Lethbridge, P. Vukusic, D. D. Deheyn and K. H. Sandhage, *Journal of Materials Chemistry*, 2012, **22**, 10435-10437.
99. M. R. Weatherspoon, Y. Cai, M. Crne, M. Srinivasarao and K. H. Sandhage, *Angewandte Chemie-International Edition*, 2008, **47**, 7921-7923.
100. M. R. Jorgensen, B. P. Yonkee and M. H. Bartl, *Scripta Materialia*, 2011, **65**, 954-957.
101. W. Zhang, D. Zhang, T. X. Fan, J. J. Gu, R. Ding, H. Wang, Q. X. Guo and H. Ogawa, *Chemistry of Materials*, 2009, **21**, 33-40.
102. W. Zhang, D. Zhang, T. X. Fan, J. Ding, Q. X. Guo and H. Ogawa, *Microporous and Mesoporous Materials*, 2006, **92**, 227-233.
103. Y. Chen, J. J. Gu, S. M. Zhu, T. X. Fan, D. Zhang and Q. X. Guo, *Applied Physics Letters*, 2009, **94**, 053901.
104. F. Song, H. L. Su, J. Han, D. Zhang and Z. X. Chen, *Nanotechnology*, 2009, **20**.
105. S. M. Zhu, X. Y. Liu, Z. X. Chen, C. J. Liu, C. L. Feng, J. J. Gu, Q. L. Liu and D. Zhang, *Journal of Materials Chemistry*, 2010, **20**, 9126-9132.
106. W. H. Peng, C. L. Zhu, S. M. Zhu, F. Yao, Y. Li and D. Zhang, *Journal of Materials Science*, 2013, **48**, 4336-4344.
107. W. H. Peng, S. M. Zhu, W. L. Wang, W. Zhang, J. J. Gu, X. B. Hu, D. Zhang and Z. X. Chen, *Advanced Functional Materials*, 2012, **22**, 2072-2080.
108. F. Yao, Q. Q. Yang, C. Yin, S. M. Zhu, D. Zhang, W. J. Moon and Y. S. Kim, *Materials Letters*, 2012, **77**, 21-24.
109. J. Han, H. L. Su, D. Zhang, J. J. Chen and Z. X. Chen, *Journal of Materials Chemistry*, 2009, **19**, 8741-8746.
110. Z. W. He, W. Zhang, W. L. Wang, M. Tassin, J. J. Gu, Q. L. Liu, S. M. Zhu, H. L. Su, C. L. Feng and D. Zhang, *Journal of Materials Chemistry B*, 2013, **1**, 1673-1677.
111. Y. W. Tan, J. J. Gu, X. N. Zang, W. Xu, K. C. Shi, L. H. Xu and D. Zhang, *Angewandte Chemie-International Edition*, 2011, **50**, 8307-8311.
112. J. W. Galusha, L. R. Richey, M. R. Jorgensen, J. S. Gardner and M. H. Bartl, *Journal of Materials Chemistry*, 2010, **20**, 1277-1284.
113. J. W. Galusha, C. K. Tsung, G. D. Stucky and M. H. Bartl, *Chemistry of Materials*, 2008, **20**, 4925-4930.
114. F. Song, H. L. Su, J. Han, J. Q. Xu and D. Zhang, *Sensors and Actuators B-Chemical*, 2010, **145**, 39-45.
115. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonovicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson and E. W. Sheppard, *Journal of the American Chemical Society*, 1992, **114**, 10834-10843.
116. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548-552.
117. C. G. Goltner and M. Antonietti, *Advanced Materials*, 1997, **9**, 431-436.
118. F. Hoffmann, M. Cornelius, J. Morell and M. Fröba, *Angewandte Chemie-International Edition*, 2006, **45**, 3216-3251.
119. C. Sanchez, C. Boissiere, D. Grosso, C. Laberty and L. Nicole, *Chemistry of Materials*, 2008, **20**, 682-737.
120. G. J. A. A. Soler-Illia and O. Azzaroni, *Chemical Society Reviews*, 2011, **40**, 1107-1150.
121. C. J. Brinker, Y. Lu, A. Sellinger and H. Fan, *Advanced Materials*, 1999, **11**, 579-585.
122. D. Grosso, F. Cagnol, G. J. A. A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois and C. Sanchez, *Advanced Functional Materials*, 2004, **14**, 309-322.
123. C. J. Brinker, *Mrs Bulletin*, 2004, **29**, 631-640.
124. P. Innocenzi, T. Kidchob, P. Falcaro and M. Takahashi, *Chemistry of Materials*, 2008, **20**, 607-614.
125. Y. Guillemin, M. Etienne, E. Sibottier and A. Walcarius, *Chemistry of Materials*, 2011, **23**, 5313-5322.
126. D. A. Doshi, N. K. Huesing, M. C. Lu, H. Y. Fan, Y. F. Lu, P. K. Simmons, B. G. Potter, A. J. Hurd and C. J. Brinker, *Science*, 2000, **290**, 107-111.
127. G. J. A. A. Soler-Illia, E. L. Crepaldi, D. Grosso, D. Durand and C. Sanchez, *Chemical Communications*, 2002, **20**, 2298-2299.
128. G. Xomeritakis, C. M. Braunbarth, B. Smarsly, N. Liu, R. Kohn, Z. Klipowicz and C. J. Brinker, *Microporous & Mesoporous Materials*, 2003, **66**, 91-101.
129. L. Malfatti, T. Kidchob, P. Falcaro, S. Costacurta, M. Piccinini, M. C. Guidi, A. Marcelli, A. Corrias, M. F. Casula, H. Amenitsch and P. Innocenzi, *Microporous And Mesoporous Materials*, 2007, **103**, 113-122.
130. Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker and C. J. Brinker, *Nature*, 1999, **398**, 223-226.
131. C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole and C. Sanchez, *Advanced Materials*, 2011, **23**, 599-623.
132. H. Y. Fan, Y. F. Lu, A. Stump, S. T. Reed, T. Baer, R. Schunk, L. V. Perez, G. P. Lopez and C. J. Brinker, *Nature*, 2000, **405**, 56-60.
133. P. D. Yang, G. Wirnsberger, H. C. Huang, S. R. Cordero, M. D. McGehee, B. Scott, T. Deng, G. M. Whitesides, B. F.

Chmelka, S. K. Buratto and G. D. Stucky, *Science*, 2000, **287**, 465-467.

134. J. B. Pang, J. N. Stuecker, Y. B. Jiang, A. J. Bhakta, E. D. Branson, P. Li, J. Cesarano, D. Sutton, P. Calvert and C. J. Brinker, *Small*, 2008, **4**, 982-989.
135. L. Nicole, C. Boissiere, D. Grosso, A. Quach and C. Sanchez, *Journal of Materials Chemistry*, 2005, **15**, 3598-3627.
136. P. Innocenzi, L. Malfatti, T. Kldchob and P. Falcaro, *Chemistry of Materials*, 2009, **21**, 2555-2564.
137. C. Boissiere, D. Grosso, H. Amenitsch, A. Gibaud, A. Coupe, N. Baccile and C. Sanchez, *Chemical Communications*, 2003, 2798-2799.
138. D. Grosso, *Journal of Materials Chemistry*, 2011, **21**, 17033-17038.
139. N. Krins, M. Faustini, B. Louis and D. Grosso, *Chemistry of Materials*, 2010, **22**, 6218-6220.
140. H. De Paz, A. Chemtob, C. Croutxe-Barghorn, S. Rigolet and B. Lebeau, *Microporous and Mesoporous Materials*, 2012, **151**, 88-92.
141. H. De Paz-Simon, A. Chemtob, F. Crest, C. Croutxe-Barghorn, L. Michelin, L. Vidal, S. Rigolet and B. Lebeau, *Rsc Advances*, 2012, **2**, 11944-11952.
142. H. De Paz-Simon, A. Chemtob, C. Croutxe-Barghorn, S. Rigolet, L. Michelin, L. Vidal and B. Lebeau, *Langmuir*, 2013, **29**, 1963-1969.
143. B. J. Melde and B. J. Johnson, *Analytical and Bioanalytical Chemistry*, 2010, **398**, 1565-1573.
144. T. Wagner, S. Haffer, C. Weinberger, D. Klaus and M. Tiemann, *Chemical Society Reviews*, 2013, **42**, 4036-4053.
145. T. H. Tran-Thi, R. Dagnelie, S. Crunaire and L. Nicole, *Chemical Society Reviews*, 2011, **40**, 621-639.
146. P. Innocenzi and L. Malfatti, *Chemical Society Reviews*, 2013, **42**, 4198-4216.
147. B. J. Melde, B. J. Johnson and P. T. Charles, *Sensors*, 2008, **8**, 5202-5228.
148. M. Vallet-Regi, F. Balas and D. Arcos, *Angewandte Chemie-International Edition*, 2007, **46**, 7548-7558.
149. M. Manzano, M. Colilla and M. Vallet-Regi, *Expert Opinion on Drug Delivery*, 2009, **6**, 1383-1400.
150. A. Walcarius, *Chemical Society Reviews*, 2013, **42**, 4098-4140.
151. J. Michaelis and C. Brauchle, *Chemical Society Reviews*, 2010, **39**, 4731-4740.
152. F. M. Ye, M. M. Collinson and D. A. Higgins, *Physical Chemistry Chemical Physics*, 2009, **11**, 66-82.
153. C. Jung, C. Hellriegel, J. Michaelis and C. Brauchle, *Advanced Materials*, 2007, **19**, 956-960.
154. J. Kirstein, B. Platschek, C. Jung, R. Brown, T. Bein and C. Brauchle, *Nature Materials*, 2007, **6**, 303-310.
155. A. Zurner, J. Kirstein, M. Doblinger, C. Brauchle and T. Bein, *Nature*, 2007, **450**, 705-709.
156. T. Lebold, C. Jung, J. Michaelis and C. Brauchle, *Nano Letters*, 2009, **9**, 2877-2883.
157. C. Jung, J. Kirstein, B. Platschek, T. Bein, M. Budde, I. Frank, K. Mullen, J. Michaelis and C. Brauchle, *Journal of the American Chemical Society*, 2008, **130**, 1638-1648.
158. T. Lebold, L. A. Muhlstein, J. Blechinger, M. Riederer, H. Amenitsch, R. Kohn, K. Peneva, K. Mullen, J. Michaelis, C. Brauchle and T. Bein, *Chemistry-a European Journal*, 2009, **15**, 1661-1672.
159. Y. Fu, F. M. Ye, W. G. Sanders, M. M. Collinson and D. A. Higgins, *Journal of Physical Chemistry B*, 2006, **110**, 9164-9170.
160. T. Lebold, J. Michaelis and C. Brauchle, *Physical Chemistry Chemical Physics*, 2011, **13**, 5017-5033.
161. R. Hernandez, A.-C. Franville, P. Minoofar, B. Dunn and J. I. Zink, *Journal of the American Chemical Society*, 2001, **123**, 1248-1249.
162. N. A. Melosh, P. Lipic, F. S. Bates, F. Wudl, G. D. Stucky, G. H. Fredrickson and B. F. Chmelka, *Macromolecules*, 1999, **32**, 4332-4342.
163. P. N. Minoofar, R. Hernandez, S. Chia, B. Dunn, J. I. Zink and A. C. Franville, *Journal of the American Chemical Society*, 2002, **124**, 14388-14396.
164. P. Minoofar, R. Hernandez, A. C. Franville, S. Y. Chia, B. Dunn and J. I. Zink, *Journal of Sol Gel Science & Technology*, 2003, **26**, 571-575.
165. F. M. Ye, D. A. Higgins and M. M. Collinson, *Journal of Physical Chemistry C*, 2007, **111**, 6772-6780.
166. C. Rottman, G. Grader, Y. De Hazan, S. Melchior and D. Avnir, *Journal of the American Chemical Society*, 1999, **121**, 8533-8543.
167. C. Rottman and D. Avnir, *Journal of the American Chemical Society*, 2001, **123**, 5730-5734.
168. C. Jung, C. Hellriegel, B. Platschek, D. Wohrle, T. Bein, J. Michaelis and C. Brauchle, *Journal of the American Chemical Society*, 2007, **129**, 5570-5579.
169. I. Y. Jeon and J. B. Baek, *Materials*, 2010, **3**, 3654-3674.
170. H. Althues, J. Henle and S. Kaskel, *Chemical Society Reviews*, 2007, **36**, 1454-1465.
171. T. Hanemann and D. V. Szabo, *Materials*, 2010, **3**, 3468-3517.
172. P. H. C. Camargo, K. G. Satyanarayana and F. Wypych, *Materials Research-Ibero-American Journal of Materials*, 2009, **12**, 1-39.
173. F. Hussain, M. Hojjati, M. Okamoto and R. E. Gorga, *J. Compos Mater.*, 2006, **40**, 1511-1575.
174. A. Okada and A. Usuki, *Macromolecular Materials and Engineering*, 2006, **291**, 1449-1476.
175. S. S. Ray and M. Okamoto, *Progress in Polymer Science*, 2003, **28**, 1539-1641.
176. D. Vollath and D. V. Szabo, *Advanced Engineering Materials*, 2004, **6**, 117-127.
177. G. Kickelbick, *Progress in Polymer Science*, 2003, **28**, 83-114.
178. R. A. Vaia and J. F. Maguire, *Chemistry of Materials*, 2007, **19**, 2736-2751.
179. W. Caseri, *Macromolecular Rapid Communications*, 2000, **21**, 705-722.
180. W. Caseri, *Chemical Engineering Communications*, 2009, **196**, 549-572.
181. W. A. Zhang and A. H. E. Muller, *Progress in Polymer Science*, 2013, **38**, 1121-1162.
182. S. W. Kuo and F. C. Chang, *Progress in Polymer Science*, 2011, **36**, 1649-1696.
183. D. Bradshaw, A. Garai and J. Huo, *Chemical Society Reviews*, 2012, **41**, 2344-2381.
184. N. Stock and S. Biswas, *Chemical Reviews*, 2012, **112**, 933-969.
185. N. Tomczak, D. Janczewski, M. Han and G. J. Vancso, *Progress in Polymer Science*, 2009, **34**, 393-430.
186. U. Schubert, *Accounts of Chemical Research*, 2007, **40**, 730-737.
187. P. Judeinstein, Schmidt, H., *Journal of Sol-Gel Science and Technology*, 1994, **3**, 189-197.
188. S. Cochet, L. Rozes, M. Popall and C. Sanchez, *Mater. Sci. Eng. C-Biomimetic Supramol. Syst.*, 2007, **27**, 1401-1405.
189. P. Judeinstein, *Chemistry of Materials*, 1992, **4**, 4-7.
190. C. R. Mayer, R. Thouvenot and T. Lalot, *Chemistry of Materials*, 2000, **12**, 257-260.
191. C. R. Mayer, R. Thouvenot and T. Lalot, *Macromolecules*, 2000, **33**, 4433-4437.
192. G. Kickelbick, D. Holzinger, C. Brick, G. Trimmel and E. Moons, *Chemistry of Materials*, 2002, **14**, 4382-4389.
193. F. Perineau, S. Pensec, C. Sassoye, F. Ribot, L. Van Lokeren, R. Willem, L. Bouteiller, C. Sanchez and L. Rozes, *Journal of materials Chemistry*, 2011, **21**, 4470-4475.
194. F. Perineau, G. J. Hu, L. Rozes, F. Ribot, C. Sanchez, C. Creton, L. Bouteiller and S. Pensec, *Journal of Polymer Science Part a-Polymer Chemistry*, 2011, **49**, 2636-2644.
195. F. Ribot, A. Lafuma, C. Eychenne-Baron and C. Sanchez, *Advanced Materials*, 2002, **14**, 1496-1499.
196. S. Trabelsi, A. Janke, R. Hassler, N. E. Zafeiropoulos, G. Fornasieri, S. Bocchini, L. Rozes, M. Stamm, J. F. Gerard and C. Sanchez, *Macromolecules*, 2005, **38**, 6068-6078.

197. L. Rozes, G. Fornasieri, S. Trabelsi, C. Creton, N. E. Zafeiropoulos, M. Stamm and C. Sanchez, *Progress in Solid State Chemistry*, 2005, **33**, 127-135.
198. U. Schubert, *Chemistry of Materials*, 2001, **13**, 3487-3494.
199. D. J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe and O. M. Yaghi, *Chemical Society Reviews*, 2009, **38**, 1257-1283.
200. G. Ferey, *Chemistry of Materials*, 2001, **13**, 3084-3098.
201. D. B. Cordes, P. D. Lickiss and F. Rataboul, *Chemical Reviews*, 2010, **110**, 2081-2173.
202. s. issue, *Chemical Society Reviews*, 2012, **41**.
203. F. Ribot, D. Minoux and C. Sanchez, *Materials Research Society Symposium proceedings*, 2000, **628**, CC2.2.
204. B. Jousseaume, M. Lahcini, M. C. Rascle, F. Ribot and C. Sanchez, *Organometallics*, 1995, **14**, 685-689.
205. F. Ribot, F. Banse, C. Sanchez, M. Lahcini and B. Jousseaume, *Journal of Sol-Gel Science and Technology*, 1997, **8**, 529-533.
206. L. Angiolini, D. Caretti, R. De Vito, F. T. Niesel, E. Salatelli, C. Carlini, F. Ribot and C. Sanchez, *J. Inorg. Organomet. Polym.*, 1997, **7**, 151-162.
207. F. Ribot, D. Veautier, S. J. Guillaudeu and T. Lalot, *Journal of Materials Chemistry*, 2005, **15**, 3973-3978.
208. G. Kickelbick and U. Schubert, *Chemische Berichte-Recueil*, 1997, **130**, 473-477.
209. G. Trimmel, B. Moraru, S. Gross, V. Di Noto and U. Schubert, *Macromolecular Symposia*, 2001, **175**, 357-366.
210. Y. Gao, N. R. Choudhury, J. Matisons, U. Schubert and B. Moraru, *Chemistry of Materials*, 2002, **14**, 4522-4529.
211. B. Moraru, N. Husing, G. Kickelbick, U. Schubert, P. Fratzl and H. Peterlik, *Chemistry of Materials*, 2002, **14**, 2732-2740.
212. V. Torma, N. Huising, H. Peterlik and U. Schubert, *Comptes Rendus Chimie*, 2004, **7**, 495-502.
213. Y. Gao, F. R. Kogler and U. Schubert, *Journal of Polymer Science Part a-Polymer Chemistry*, 2005, **43**, 6586-6591.
214. Y. Gao, F. R. Kogler, H. Peterlik and U. Schubert, *Journal of Materials Chemistry*, 2006, **16**, 3268-3276.
215. F. Faccini, H. Fric, U. Schubert, E. Wendel, O. Tsetsgee, K. Mueller, H. Bertagnolli, A. Venzo and S. Gross, *Journal of Materials Chemistry*, 2007, **17**, 3297-3307.
216. P. Heinz, M. Puchberger, M. Bendova, S. O. Baumann and U. Schubert, *Dalton Transactions*, 2010, **39**, 7640-7644.
217. P. Toledano, M. In and C. Sanchez, *Comptes Rendus De L Academie Des Sciences Serie Ii*, 1991, **313**, 1247-1253.
218. P. D. Moran, C. E. F. Rickard, G. A. Bowmaker, R. P. Cooney, J. R. Bartlett and J. L. Woolfrey, *Inorganic Chemistry*, 1998, **37**, 1417-1419.
219. C. Sanchez, M. In, P. Toledano and P. Griesmar, *Mat. Res. Soc. Symp. Proc*, 1992, **271**, 669.
220. G. Guerrero, M. Mehring, P. H. Mutin, F. Dahan and A. Vioux, *J. Chem. Soc.-Dalton Trans.*, 1999, 1537-1538.
221. M. Mehring, G. Guerrero, F. Dahan, P. H. Mutin and A. Vioux, *Inorganic Chemistry*, 2000, **39**, 3325-3332.
222. F. Palacio, P. Oliete, U. Schubert, I. Mijatovic, N. Husing and H. Peterlik, *Journal of Materials Chemistry*, 2004, **14**, 1873-1878.
223. S. Willemin, B. Donnadieu, L. Lecren, B. Henner, R. Clerac, C. Guerin, A. Meyer, A. V. Pokrovskii and J. Larionova, *New Journal of Chemistry*, 2004, **28**, 919-928.
224. M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez and G. Ferey, *Journal of the American Chemical Society*, 2009, **131**, 10857-10859.
225. C. Serre, F. Millange, S. Surble and G. Ferey, *Angewandte Chemie-International Edition*, 2004, **43**, 6286-6289.
226. V. Guillerm, S. Gross, C. Serre, T. Devic, M. Bauer and G. Ferey, *Chemical Communications*, 2010, **46**, 767-769.
227. M. Eshel, A. Bino, I. Felner, D. C. Johnston, M. Luban and L. L. Miller, *Inorganic Chemistry*, 2000, **39**, 1376-1380.
228. Y. H. Fu, D. R. Sun, Y. J. Chen, R. K. Huang, Z. X. Ding, X. Z. Fu and Z. H. Li, *Angewandte Chemie-International Edition*, 2012, **51**, 3364-3367.
229. C. H. Hendon, D. Tiana, M. Fontecave, C. Sanchez, L. D'Arras, C. Sassoye, L. Rozes, C. Mellot-Draznieks and A. Walsh, *Journal of the American Chemical Society*, 2013, **135**, 10942-10945.
230. F. Perineau, S. Pensec, C. Sanchez, C. Creton, L. Rozes and L. Bouteiller, *Polymer Chemistry*, 2011, **2**, 2785-2788.
231. S. Eslava, A. C. Papageorgiou, S. K. Beaumont, G. Kyriakou, D. S. Wright and R. M. Lambert, *Chemistry of Materials*, 2010, **22**, 5174–5178.
232. G. S. Constable, A. J. Lesser and E. B. Coughlin, *Macromolecules*, 2004, **37**, 1276-1282.
233. H. Chen, L. Xie, H. Lu and Y. Yang, *Journal of Materials Chemistry*, 2007, **17**, 1258-1261.
234. S. Perruchas, S. Flores, B. Jousselme, E. Lobkovsky, H. Abruna and F. J. DiSalvo, *Inorganic Chemistry*, 2007, **46**, 8976-8987.
235. V. Di Noto, A. B. Boeer, S. Lavina, C. A. Muryn, M. Bauer, G. A. Timco, E. Negro, M. Rancan, R. E. P. Winpenny and S. Gross, *Advanced Functional Materials*, 2009, **19**, 3226-3236.
236. A. I. Kuznetsov, O. Kameneva, N. Bityurin, L. Rozes, C. Sanchez and A. Kanaev, *Physical Chemistry Chemical Physics*, 2009, **11**, 1248-1257.
237. J. B. Benedict and P. Coppens, *Journal of the American Chemical Society*, 2010, **132**, 2938-2944.
238. R. C. I. Snoeberger, K. J. Young, J. Tang, L. J. Allen, R. H. Crabtree, G. W. Brudvig, P. Coppens, S. B. Victor and J. B. Benedict, *Journal of the American Chemical Society*, 2012, **134**, 8911-8917.
239. J. P. Corden, W. Errington, P. Moore, M. G. Partridge and M. G. H. Wallbridge, *Dalton Transactions*, 2004, 1846-1851.
240. M. D. Hager, P. Greil, C. Leyens, S. van der Zwaag and U. S. Schubert, *Advanced Materials*, 2010, **22**, 5424-5430.
241. S. D. Bergman and F. Wudl, *Journal of Materials Chemistry*, 2008, **18**, 41-62.
242. K. A. Williams, D. R. Dreyer and C. W. Bielawski, *Mrs Bulletin*, 2008, **33**, 759-765.
243. J. P. Youngblood, N. R. Sottos and C. Extrand, *Mrs Bulletin*, 2008, **33**, 732-741.
244. M. J. Harrington, A. Masic, N. Holten-Andersen, J. H. Waite and P. Fratzl, *Science*, 2010, **328**, 216-220.
245. S. Krauss, T. H. Metzger, P. Fratzl and M. J. Harrington, *Biomacromolecules*, 2013, **14**, 1520-1528.
246. S. R. White, N. R. Sottos, P. H. Geubelle, J. S. Moore, M. R. Kessler, S. R. Sriram, E. N. Brown and S. Viswanathan, *Nature*, 2001, **409**, 794-797.
247. J. L. Yang, M. W. Keller, J. S. Moore, S. R. White and N. R. Sottos, *Macromolecules*, 2008, **41**, 9650-9655.
248. X. X. Chen, M. A. Dam, K. Ono, A. Mal, H. B. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698-1702.
249. A. Rekondo, R. Martin, A. Ruiz de Luzuriaga, G. Cabanero, H. J. Grande and I. Odriozola, *Materials Horizons*, 2014, **1**, 237-240.
250. J. Fox, J. J. Wie, B. W. Greenland, S. Burattini, W. Hayes, H. M. Colquhoun, M. E. Mackay and S. J. Rowan, *Journal of the American Chemical Society*, 2012, **134**, 5362-5368.
251. P. Cordier, F. Tournilhac, C. Soulie-Ziakovic and L. Leibler, *Nature*, 2008, **451**, 977-980.
252. F. Potier, A. Guinault, S. Delalande, C. Sanchez, F. Ribot and L. Rozes, *Polymer Chemistry*, 2014, DOI: 10.1039/C1034PY00172A.
253. P. G. Bruce, B. Scrosati and J. M. Tarascon, *Angewandte Chemie-International Edition*, 2008, **47**, 2930-2946.
254. P. Gomez-Romero, *Advanced Materials*, 2001, **13**, 163-174.
255. C. Laberty-Robert, K. Valle, F. Pereira and C. Sanchez, *Chemical Society Reviews*, 2011, **40**, 961-1005.
256. F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature*, 1998, **394**, 456-458.
257. F. Croce, R. Curini, A. Martinelli, L. Persi, F. Ronci, B. Scrosati and R. Caminiti, *Journal of Physical Chemistry B*, 1999, **103**, 10632-10638.
258. F. Croce and B. Scrosati, in *Advanced Membrane Technology*, eds. N. N. Li, E. Drioli, W. S. W. Ho and G. G. Lipscomb2003, vol. 984, pp. 194-207.
259. A. S. Arico, P. Bruce, B. Scrosati, J. M. Tarascon and W. Van Schalkwijk, *Nature Materials*, 2005, **4**, 366-377.

260. G. B. Appetecchi, F. Croce, L. Persi, F. Ronci and B. Scrosati, *Electrochimica Acta*, 2000, **45**, 1481-1490.

261. F. Croce, L. Settimi and B. Scrosati, *Electrochemistry Communications*, 2006, **8**, 364-368.

262. V. Bolis, G. Magnacca, G. Cerrato and C. Morterra, *Langmuir*, 1997, **13**, 888-894.

263. R. J. Gillespi, *Accounts of Chemical Research*, 1968, **1**, 202-&.

264. G. Liu, M. T. Reinhout and G. L. Baker, *Solid State Ionics*, 2004, **175**, 721-724.

265. M. Dolle, L. Sannier, B. Beaudoin, M. Trentin and J. M. Tarascon, *Electrochemical and Solid State Letters*, 2002, **5**, A286-A289.

266. J. M. Tarascon, A. S. Gozdz, C. Schmutz, F. Shokoohi and P. C. Warren, *Solid State Ionics*, 1996, **86-8**, 49-54.

267. J. Y. Song, Y. Y. Wang and C. C. Wan, *Journal of Power Sources*, 1999, **77**, 183-197.

268. M. C. Borghini, M. Mastragostino, S. Passerini and B. Scrosati, *Journal of the Electrochemical Society*, 1995, **142**, 2118-2121.

269. J. Fan and P. S. Fedkiw, *Journal of the Electrochemical Society*, 1997, **144**, 399-408.

270. S. K. Das, S. S. Mandal and A. J. Bhattacharyya, *Energy & Environmental Science*, 2011, **4**, 1391-1399.

271. E. Strauss, D. Golodnitsky and E. Peled, *Electrochemical and Solid State Letters*, 1999, **2**, 115-117.

272. N. S. Choi, Y. M. Lee, B. H. Lee, J. A. Lee and J. K. Park, *Solid State Ionics*, 2004, **167**, 293-299.

273. J. Sun, P. Bayley, D. R. MacFarlane and M. Forsyth, *Electrochimica Acta*, 2007, **52**, 7083-7090.

274. J. Nordstrom, A. Matic, J. Z. Sun, M. Forsyth and D. R. MacFarlane, *Soft Matter*, 2010, **6**, 2293-2299.

275. Y. S. Lee, S. H. Ju, J. H. Kim, S. S. Hwang, J. M. Choi, Y. K. Sun, H. Kim, B. Scrosati and D. W. Kim, *Electrochemistry Communications*, 2012, **17**, 18-21.

276. A. Fernicola, B. Scrosati and H. Ohno, *Ionics*, 2006, **12**, 95-102.

277. Gillespi.Rj, *Accounts of Chemical Research*, 1968, **1**, 202-&.

278. A. Steck, 1995.

279. G.-R. P. a. S. C., *Functional Hybrid Materials*, Wiley-VCH, Weinheim2006.

280. K. A. a. Y. M. L. E. Ruiz Hitzky, *Bio-inorganic Hybrid, Nanomaterials*2008.

281. J. I. Bregman and R. S. Braman, *Journal of Colloid Science*, 1965, **20**, 913-&.

282. A. G., *Semaine sur la thème Membranes Biologiques et Artificielles et la Desalination de l'eau*1975.

283. G. Alberti, M. Casciola, U. Costantino and G. Levi, *Journal of Membrane Science*, 1978, **3**, 179-190.

284. G. Alberti, M. Casciola and U. Costantino, *Journal of Membrane Science*, 1983, **16**, 137-149.

285. C. U. a. P. R. Alberti G., 1989.

286. A. G., 1992.

287. H. T. Wang, B. A. Holmberg, L. M. Huang, Z. B. Wang, A. Mitra, J. M. Norbeck and Y. S. Yan, *Journal of Materials Chemistry*, 2002, **12**, 834-837.

288. *rance Pat.,* 2007.

289. F. Niepceron, B. Lafitte, H. Galiano, J. Bigarre, E. Nicol and J. F. Tassin, *Journal of Membrane Science*, 2009, **338**, 100-110.

290. K. A. Mauritz, I. D. Stefanithis, S. V. Davis, R. W. Scheetz, R. K. Pope, G. L. Wilkes and H. H. Huang, *Journal of Applied Polymer Science*, 1995, **55**, 181-190.

291. K. A. Mauritz, *Macromolecules*, 1989, **22**, 4483-4488.

292. Q. Deng, R. B. Moore and K. A. Mauritz, *Chemistry of Materials*, 1995, **7**, 2259-2268.

293. Q. Deng, W. Jarrett, R. B. Moore and K. A. Mauritz, *Journal of Sol-Gel Science and Technology*, 1996, **7**, 177-190.

294. K. A. Mauritz and M. K. Hassan, *Polymer Reviews*, 2007, **47**, 543-565.

295. K. Valle, P. Belleville, F. Pereira and C. Sanchez, *Nature Materials*, 2006, **5**, 107-111.

296. O. Sel, C. Laberty-Robert, T. Azais and C. Sanchez, *Physical Chemistry Chemical Physics*, 2009, **11**, 3733-3741.

297. F. Pereira, A. Chan, K. Valle, P. Palmas, J. Bigarre, P. Belleville and C. Sanchez, *Chemistry-an Asian Journal*, 2011, **6**, 1217-1224.

298. O. Sel, A. Soules, B. Ameduri, B. Boutevin, C. Laberty-Robert, G. Gebel and C. Sanchez, *Advanced Functional Materials*, 2010, **20**, 1090-1098.

299. O. Sel, T. Azais, M. Marechal, G. Gebel, C. Laberty-Robert and C. Sanchez, *Chemistry-an Asian Journal*, 2011, **6**, 2992-3000.

300. V. Maneeratana, J. D. Bass, T. Azais, A. Patissier, K. Valle, M. Marechal, G. Gebel, C. Laberty-Robert and C. Sanchez, *Advanced Functional Materials*, 2013, **23**, 2872-2880.

301. P. Verma and P. Novak, *Carbon*, 2012, **50**, 2599-2614.

302. C. Martin, M. Alias, F. Christien, O. Crosnier, D. Belanger and T. Brousse, *Advanced Materials*, 2009, **21**, 4735-+.

303. C. Martin, O. Crosnier, R. Retoux, D. Belanger, D. M. Schleich and T. Brousse, *Advanced Functional Materials*, 2011, **21**, 3524-3530.

304. M. Pandurangappa, N. S. Lawrence and R. G. Compton, *Analyst*, 2002, **127**, 1568-1571.

305. K. Kalinathan, D. P. DesRoches, X. R. Liu and P. G. Pickup, *Journal of Power Sources*, 2008, **181**, 182-185.

306. G. de Combarieu, M. Morcrette, F. Millange, N. Guillou, J. Cabana, C. P. Grey, I. Margiolaki, G. Ferey and J. M. Tarascon, *Chemistry of Materials*, 2009, **21**, 1602-1611.

307. G. Pognon, T. Brousse and D. Belanger, *Carbon*, 2011, **49**, 1340-1348.

308. M. Delamar, R. Hitmi, J. Pinson and J. M. Saveant, *Journal of the American Chemical Society*, 1992, **114**, 5883-5884.

309. D. Belanger and J. Pinson, *Chemical Society Reviews*, 2011, **40**, 3995-4048.

310. A. Morozan and F. Jaouen, *Energy & Environmental Science*, 2012, **5**, 9269-9290.

311. A. Banerjee, U. Singh, V. Aravindan, M. Srinivasan and S. Ogale, *Nano Energy*, 2013, **2**, 1158-1163.

312. R. Demir-Cakan, M. Morcrette, F. Nouar, C. Davoisne, T. Devic, D. Gonbeau, R. Dominko, C. Serre, G. Ferey and J. M. Tarascon, *Journal of the American Chemical Society*, 2011, **133**, 16154-16160.

313. S. Kitagawa, R. Kitaura and S. Noro, *Angewandte Chemie-International Edition*, 2004, **43**, 2334-2375.

314. W. J. Song, Z. F. Chen, C. R. K. Glasson, K. Hanson, H. L. Luo, M. R. Norris, D. L. Ashford, J. J. Concepcion, M. K. Brennaman and T. J. Meyer, *Chemphyschem*, 2012, **13**, 2882-2890.

315. Y. X. Zhao, J. R. Swierk, J. D. Megiatto, B. Sherman, W. J. Youngblood, D. D. Qin, D. M. Lentz, A. L. Moore, T. A. Moore, D. Gust and T. E. Mallouk, *Proceedings of the National Academy of Sciences of the United States of America*, 2012, **109**, 15612-15616.

316. Y. Gao, X. Ding, J. H. Liu, L. Wang, Z. K. Lu, L. Li and L. C. Sun, *Journal of the American Chemical Society*, 2013, **135**, 4219-4222.

317. Z. Q. Ji, M. F. He, Z. J. Huang, U. Ozkan and Y. Y. Wu, *Journal of the American Chemical Society*, 2013, **135**, 11696-11699.

318. J. M. Gardner, M. Beyler, M. Karnahl, S. Tschierlei, S. Ott and L. Hammarstrom, *Journal of the American Chemical Society*, 2012, **134**, 19322-19325.

319. L. Li, L. L. Duan, F. Y. Wen, C. Li, M. Wang, A. Hagfeld and L. C. Sun, *Chemical Communications*, 2012, **48**, 988-990.

320. P. Judeinstein and C. Sanchez, *Journal of Materials Chemistry*, 1996, **6**, 511-525.

321. www.schott.com.

322. C. Sanchez, B. Lebeau, F. Chaput and J. P. Boilot, *Advanced Materials*, 2003, **15**, 1969-1994.

323. Essilor, *Materials & Treatments*, Ophthalmic Optics Files, http://www.varilux-university.org2010.

324. P. Rivera Gil, D. Huhn, L. L. del Mercato, D. Sasse and W. J. Parak, *Pharmacological Research*, 2010, **62**, 115-125.

325. S. Laurent, D. Forge, M. Port, A. Roch, C. Robic, L. V. Elst and R. N. Muller, *Chemical Reviews*, 2008, **108**, 2064-2110.

326. *Sol-Gel Technologies*, http://www.sol-gel.com.

327. N. Lapidot, O. Gans, F. Biagini, L. Sosonkin and C. Rottman, *Eurocosmetics*, 2000, **1**, 20.
328. N. Lapidot, O. Gans, F. Biagini, L. Sosonkin and C. Rottman, *Journal of Sol-Gel Science and Technology*, 2003, **26**, 67-72.
329. M. A. Aegerter, N. Leventis and M. M. Koebel, *Aerogels Handbook*, Springer2011.
330. WO/1994/25149, 1994.
331. D. M. Smith, R. Deshpande and C. J. Brinker, *Mater. Res. Soc. Symp. Proc.*, 1992, **271**, 567-572.
332. S. J. Kramer, F. Rubio-Alonso and J. D. Mackenzie, *Mater. Res. Soc. Symp. Proc.*, 1996, **435**, 295-300.
333. K. Kanamori, M. Aizawa, K. Nakanishi and T. Hanada, *Advanced Materials*, 2007, **19**, 1589-+.
334. A. V. Rao, N. D. Hegde and H. Hirashima, *Journal of Colloid and Interface Science*, 2007, **305**, 124-132.
335. N. Leventis, C. Sotiriou-Leventis, G. H. Zhang and A. M. M. Rawashdeh, *Nano Letters*, 2002, **2**, 957-960.
336. M. A. B. Meador, E. F. Fabrizio, F. Ilhan, A. Dass, G. H. Zhang, P. Vassilaras, J. C. Johnston and N. Leventis, *Chemistry of Materials*, 2005, **17**, 1085-1098.
337. U. F. Ilhan, E. F. Fabrizio, L. McCorkle, D. A. Scheiman, A. Dass, A. Palczer, M. B. Meador, J. C. Johnston and N. Leventis, *Journal of Materials Chemistry*, 2006, **16**, 3046-3054.
338. A. B. Morgan, *Polym. Adv. Technol.*, 2006, **17**, 206-217.
339. H. Zou, S. S. Wu and J. Shen, *Chemical Reviews*, 2008, **108**, 3893-3957.
340. B. Chen, J. R. G. Evans, H. C. Greenwell, P. Boulet, P. V. Coveney, A. A. Bowden and A. Whiting, *Chemical Society Reviews*, 2008, **37**, 568-594.
341. E. P. Giannelis, *Advanced Materials*, 1996, **8**, 29-&.
342. M. Alexandre and P. Dubois, *Materials Science & Engineering R-Reports*, 2000, **28**, 1-63.
343. E. T. Thostenson, C. Y. Li and T. W. Chou, *Composites Science and Technology*, 2005, **65**, 491-516.
344. S. C. Tjong, *Materials Science & Engineering R-Reports*, 2006, **53**, 73-197.
345. C. H. M. Hofman-Caris, *New Journal of Chemistry*, 1994, **18**, 1087-1096.
346. E. Bourgeat-Lamy, *Journal of Nanosciences and Nanotechnologies*, 2002, **2**, 1-24.
347. E. Bourgeat-Lami, in *Encyclopedia of Nanoscience and Nanotechnology*, ed. H. S. Nalwa, American Scientific Publishers2004, vol. 8, pp. 305-332.
348. M. Daniel and C. Janin, *Actual Chim.*, 2010, 8-13.
349. C. Janin, *Actual Chim.*, 1999, 67-71.
350. Y. Fukushima and S. Inagaki, *Journal of Inclusion Phenomena*, 1987, **5**, 473-482.
351. US 4739007, 1987.
352. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *Journal of Materials Research*, 1993, **8**, 1185-1189.
353. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *Journal of Materials Research*, 1993, **8**, 1179-1184.
354. *Plastics, Additives and Compounding*, 2002, **4**, 30-33.
355. A. Grinthal and J. Aizenberg, *Chemical Society Reviews*, 2013, **42**, 7072-7085.