Applications of hybrid organic–inorganic nanocomposites

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Organic–inorganic hybrid materials do not represent only a creative alternative to design new materials and compounds for academic research, but their improved or unusual features allow the development of innovative industrial applications. Nowadays, most of the hybrid materials that have already entered the market are synthesised and processed by using conventional soft chemistry based routes developed in the eighties. These processes are based on: a) the copolymerisation of functional organosilanes, macromonomers, and metal alkoxides, b) the encapsulation of organic components within sol–gel derived silica or metallic oxides, c) the organic functionalisation of nanofillers, nanoclays or other compounds with lamellar structures, *etc*. The chemical strategies (self-assembly, nanobuilding block approaches, hybrid MOF (Metal Organic Frameworks), integrative synthesis, coupled processes, bio-inspired strategies, *etc.*) offered nowadays by academic research allow, through an intelligent tuned coding, the development of a new vectorial chemistry, able to direct the assembling of a large variety of structurally well defined nano-objects into complex hybrid architectures hierarchically organised in terms of structure and functions. Looking to the future, there is no doubt that these new generations of hybrid materials, born from the very fruitful activities in this research field, will open a land of promising applications in many areas: optics, electronics, ionics, mechanics, energy, environment, biology, medicine for example as membranes and separation devices, functional smart coatings, fuel and solar cells, catalysts, sensors, *etc*.

I. Introduction

For the past five hundred million years nature has produced materials with remarkable properties and features such as the beautifully carved structures found in radiolaria or diatoms (Fig. 1).[1,2] Another of nature's remarkable features is its ability to combine at the nanoscale (bio) organic and inorganic components allowing the construction of smart natural materials that found a compromise between different properties or functions (mechanics, density, permeability, colour,

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hydrophobia, *etc.*). Such a high level of integration associates several aspects: miniaturisation whose object is to accommodate a maximum of elementary functions in a small volume, hybridisation between inorganic and organic components optimizing complementary possibilities, functions and hierarchy.[1] Current examples of natural organic–inorganic composites are crustacean carapaces or mollusc shells and bone or teeth tissues in vertebrates.

As far as man-made materials are concerned, the possibility to combine properties of organic and inorganic components for materials design and processing is a very old challenge that likely started since ages (Egyptian inks, green bodies of china ceramics, prehistoric frescos, *etc.*).

However, the so-called hybrid organic–inorganic materials[3–11] are not simply physical mixtures. They can be broadly defined as nanocomposites with organic and inorganic components, intimately mixed. Indeed, hybrids are either homogeneous systems derived from monomers and miscible organic and inorganic components, or heterogeneous systems (nanocomposites) where at least one of the components' domains has a dimension ranging from some Å to several nanometers.[8c] It is obvious that properties of these materials are not only the sum of the individual contributions of both phases, but the role of the inner interfaces could be predominant. The nature of the interface has been used to grossly divide these materials into two distinct classes.[8c] In *class I*, organic and inorganic components are embedded and only weak bonds (hydrogen, van der Waals or ionic bonds) give the cohesion to the whole structure. In *class II* materials, the two phases are linked together through strong chemical bonds (covalent or iono-covalent bonds).

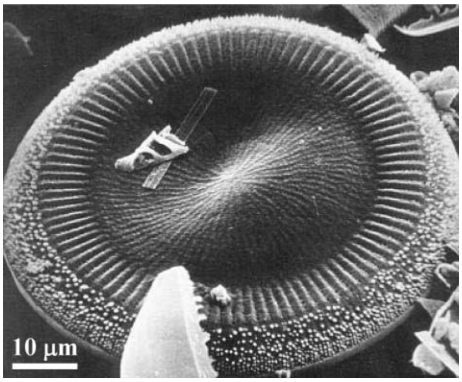


Fig. 1 Scanning electron micrography of the silicic skeleton of a diatom, showing a complex and finely carved morphology.[1]

Maya blue is a beautiful example of a remarkable quite old man-made class I hybrid material whose conception was the fruit of an ancient serendipitous discovery. Ancient Maya fresco paintings are characterized by bright blue colors that had been miraculously preserved (Fig. 2).[12,13]

That particular Maya blue pigment had withstood more than twelve centuries of a harsh jungle environment looking almost as fresh as when it was used in the 8th century. Maya blue is indeed a robust pigment, not only resisting biodegradation, but showing also unprecedented stability when exposed to acids, alkalis and organic solvents.

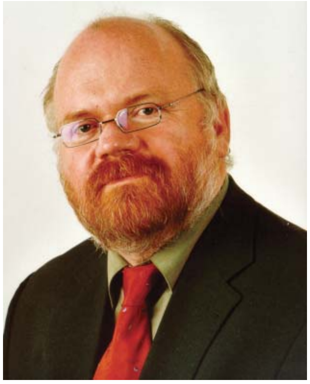
Beatriz Julián-López

Dr Beatriz Julián-López was born in 1977. She obtained her B.Sc. degree in chemistry (1995–1999) at the Jaume I University of Castellón (Spain), where she also received her Ph.D. in Chemistry of Materials (1999–2003) with the European Mention. Her first work was focused on the synthesis of ceramic pigments (by solid state and non-conventional methods) but during her Ph.D., carried out under the supervision of Dr E. Cordoncillo and Dr P. Escribano (Castellón) and Dr C. Sanchez (Paris), she specialized in the synthesis and characterization of sol–gel hybrid organic–inorganic materials for optical applications. In 2004 she moved to Paris, where she is currently undertaking a post-doctoral fellowship at Dr C. Sanchez's Laboratory (University of Pierre and Marie Curie). Her main interest is the development of novel multifunctional hybrid organic–inorganic materials, textured at different scales, by combining sol–gel and self-assembling processes, for optical and biomedical applications.

Philippe Belleville

Philippe Belleville is head of the CEA sol–gel laboratory. He is the author of more than 30 publications and more than 20 patents. He was successful in leading 6 technology transfers. He has been a member of the Sol–Gel Optics Committee since 2000. He was the recipient of the 2003 Ulrich Award for Excellence in Sol–Gel Technology.

Dr Michael Popall, born 26/06/55, chemist, has more than 20 years experience in applied materials research. He received his PhD in 1986 in metal–organic chemistry, at Technical University Munich. He is now head of business-unit microsystems and mobile power supply at Fraunhofer ISC. His materials research is on organic–inorganic hybrids, ORMOCER$^{®}$*s, for optical, dielectric and electrochemical applications. He received the German Science Price in 2002 (Stifter foundation) for a European project on ORMOCER*$^{®}$ *based interconnection technology, and the NanoTech Future Award 2005 (Tokyo, Japan) in micromachining for ORMOCER*$^{®}$ *based micro-lens arrays.*



Michael Popall

Fig. 2 Computer enhanced Mayan Warrior from Bonampak (Mexico).[12,13]

Maya blue is a hybrid organic–inorganic material with molecules of the natural blue indigo encapsulated within the channels of a clay mineral known as palygorskite. It is a man-made material that combines the color of the organic pigment and the resistance of the inorganic host, a synergic material, with properties and performance well beyond those of a simple mixture of its components.

Considering the industrial era, successful commercial hybrid organic–inorganic polymers have been part of manufacturing technology since the 1950s.[14] Paints are a good link between Mayas and modern applications of hybrids. Indeed, some of the oldest and most famous organic–inorganic industrial representatives are certainly coming from the paint industries, where inorganic nano-pigments are suspended in organic mixtures (solvents, surfactants, *etc.*). While the name of "hybrid" materials was not evoked at that time, the wide increase of work on organic–inorganic structures was pursued with the development of the polymer industry. The concept of "hybrid organic–inorganic" nanocomposites exploded in the eighties with the expansion of soft inorganic chemistry processes. Indeed the mild synthetic conditions offered by the sol–gel process (metallo-organic precursors, organic solvents, low processing temperatures, processing versatility of the colloidal state) allow the mixing of inorganic and organic components at the nanometric scale.[3–11] Since then, the study of so-called functional hybrid nanocomposites became a mushrooming field of investigation yielding innovative advanced materials with high added value. These materials being at the interface of organic and inorganic realms are highly versatile offering a wide range of possibilities to elaborate tailor-made materials in terms of processing and chemical and physical properties.[11]

Today, this potential is becoming real and many hybrid materials are entering niche markets that should expand in the future because new and stricter requirements are now being set up to achieve greater harmony between the environment and human activities. New materials and systems produced by man must in future aim at higher levels of sophistication and miniaturisation, be recyclable and respect the environment, be reliable and consume less energy. Without any doubt, hybrid materials will soon generate smart membranes, new catalysts and sensors, new generation of photovoltaic and fuel cells, smart microelectronic, micro-optical and photonic components and systems, or intelligent therapeutic vectors that combine targeting, imaging, therapy and controlled release properties.

This review summarizes the general chemical pathways to prepare hybrid materials and presents the most striking examples of applications of functional hybrids, selecting them among the existing prototypes or commercially available hybrid materials.

II. General strategies for the design of functional hybrids

Independently of the types or applications, as well as the nature of the interface between organic and inorganic components, a second important feature in the tailoring of hybrid networks concerns the chemical pathways that are used to design a given hybrid material. General strategies for the synthesis of sol–gel derived hybrid materials have been already discussed in details in several reviews.[7,8,11] The main chemical routes for all type of hybrids are schematically represented in Fig. 3.

Path A corresponds to very convenient soft chemistry based routes including conventional sol–gel chemistry, the use of specific bridged and polyfunctional precursors and hydrothermal synthesis.

Route A1: *Via* **conventional sol–gel pathways** amorphous hybrid networks are obtained through hydrolysis of organically modified metal alkoxides (*vide infra* section III) or metal halides condensed with or without simple metallic alkoxides. The solvent may or may not contain a specific organic molecule, a biocomponent or polyfunctional polymers that can be crosslinkable or that can interact or be trapped within the inorganic components through a large set of fuzzy interactions (H-bonds, π–π interactions, van der Waals). These strategies are simple, low cost and yield amorphous nanocomposite hybrid materials. These materials, exhibiting infinite microstructures, can be transparent and easily shaped as films or bulks. They are generally polydisperse in size and locally heterogeneous in chemical composition. However, they are cheap, very versatile, present many interesting properties and consequently they give rise to many commercial products shaped as films, powders or monoliths. These commercial products and their field of application will be discussed in section III-2. Better academic understanding and control of the local and semi-local structure of the hybrid materials and their degree of organization are important issues, especially if in the future tailored properties are sought. The main approaches that are used to achieve such a control of the materials structure are also schematized in Fig. 3.

Route A2: The use of **bridged precursors such as silsesquioxanes** $X_3Si–R'–SiX_3$ (R' is an organic spacer, X = Cl, Br, OR) allow the formation of homogeneous molecular hybrid organic–inorganic materials which have a better degree of

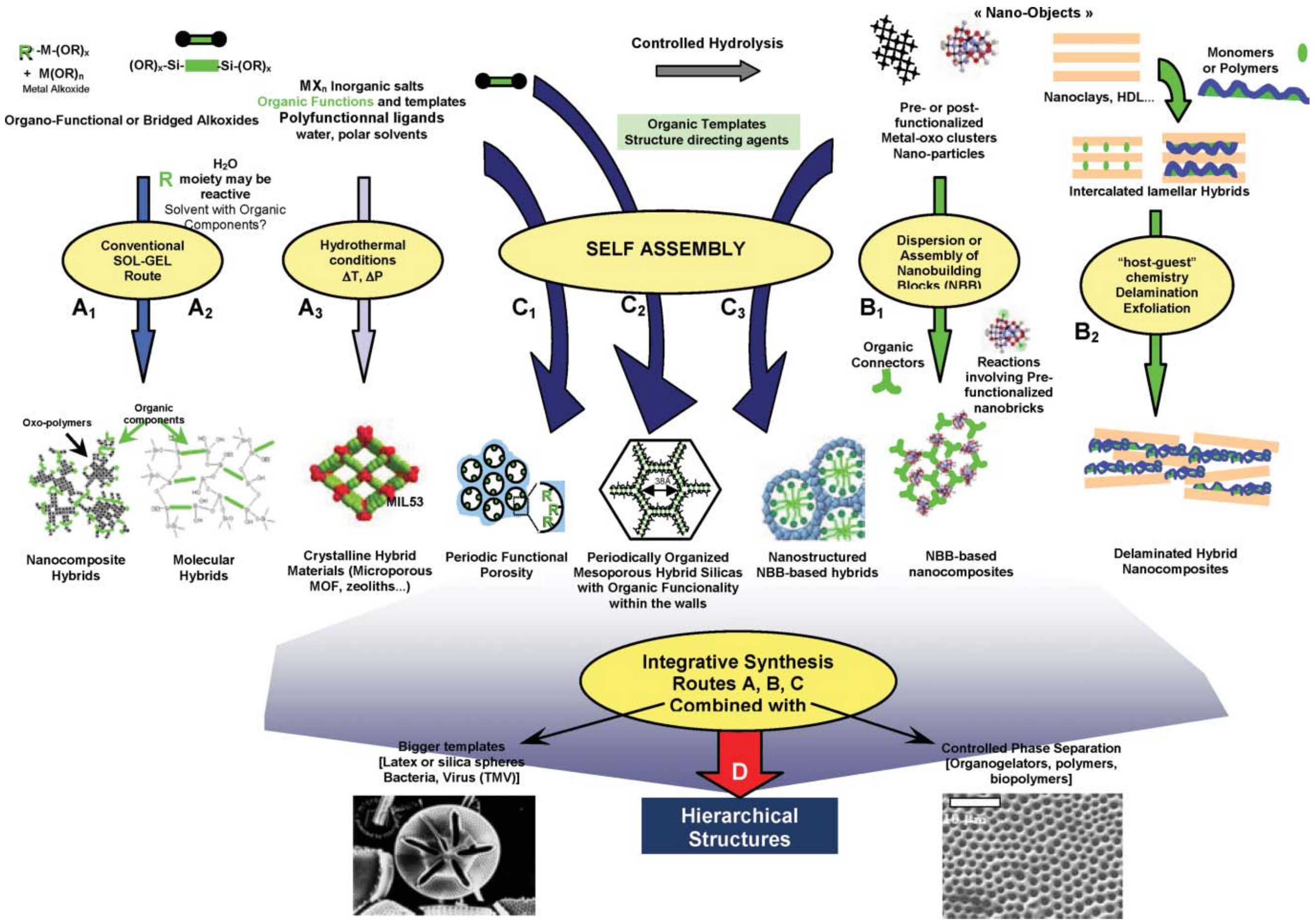


Fig. 3 Scheme of the main chemical routes for the synthesis of organic–inorganic hybrids.

local organisation.[8g,e,15] In recent work, the organic spacer has been complemented by using two terminal functional groups (urea type).[15–17] The combination within the organic bridging component of aromatic or alkyl groups and urea groups allows better self-assembly through the capability of the organic moieties to establish both strong hydrogen bond networks and efficient packing *via* π–π or hydrophobic interactions.[15–17]

Route A3: Hydrothermal synthesis in polar solvents (water, formamide, *etc.*) in the presence of organic templates had given rise to numerous zeolites with an extensive number of applications in the domain of adsorbents or catalysts. More recently a new generation of crystalline microporous hybrid solids have been discovered by several groups (Yaghi,[18] Ferey,[19–23] Cheetham and Rao[24]). These hybrid materials exhibit very high surface areas (from 1000 to 4500 $m^2 g^{-1}$) and present hydrogen uptakes of about 3.8 wt% at 77 K.[18–24] Moreover, some of these new hybrids can also present magnetic or electronic properties.[20,25] These hybrid MOF (Metal Organic Frameworks) are very promising candidates for catalytic and gas adsorption based applications.[18]

Path B corresponds to *the assembling* (**route B1**) *or the dispersion* (**route B2**) *of well-defined nanobuilding blocks* (NBB) which consists of perfectly calibrated preformed objects that keep their integrity in the final material.[7] This is a suitable method to reach a better definition of the inorganic component. These NBB can be clusters, organically pre- or post- functionalized nanoparticles (metallic oxides, metals, chalcogenides, *etc.*), nano-core–shells[26] or layered compounds (clays, layered double hydroxides, lamellar phosphates, oxides or chalcogenides) able to intercalate organic components.[27–29] These NBB can be capped with polymerizable ligands or connected through organic spacers, like telechelic molecules or polymers, or functional dendrimers (Fig. 3). The use of highly pre-condensed species presents several advantages:

• they exhibit a lower reactivity towards hydrolysis or attack of nucleophilic moieties than metal alkoxides;

• the nanobuilding components are nanometric, monodispersed, and with better defined structures, which facilitates the characterization of the final materials.

The variety found in the nanobuilding blocks (nature, structure, and functionality) and links allows one to build an amazing range of different architectures and organic–inorganic interfaces, associated with different assembling strategies. Moreover, the step-by-step preparation of these materials usually allows for high control over their semi-local structure.

One important set of the NNB based hybrid materials that are already on the market are those resulting from the intercalation, swelling, and exfoliation of nanoclays by organic polymers. Their applications will be described in section IV.

Path C Self *assembling procedures*. In the last ten years, a new field has been explored, which corresponds to the organization or the texturation of growing inorganic or hybrid networks, *templated growth by organic surfactants* (Fig. 3, **Route C1**).[30–36] The success of this strategy is also clearly related to the ability that materials scientists have to control and tune hybrid interfaces. In this field, hybrid organic–inorganic phases are very interesting due to the versatility they demonstrate in the building of a whole continuous range of nanocomposites, from ordered dispersions of inorganic bricks in a hybrid matrix to highly controlled nanosegregation of organic polymers within inorganic matrices. In the latter case, one of the most striking examples is the synthesis of mesostructured hybrid networks.[33] A recent strategy developed by several groups consists of the *templated growth* (with surfactants) of mesoporous hybrids *by using bridged silsesquioxanes as precursors* (Fig. 3, **Route C2**). This approach yields a new class of periodically organised mesoporous hybrid silicas with organic functionality within the walls. These nanoporous materials present a high degree of order and their mesoporosity is available for further organic functionalisation through surface grafting reactions.[37]

Route C3 corresponds to the *combination of self-assembly and NBB approaches*.[7] Strategies combining the nanobuilding block approach with the use of organic templates that self-assemble and allow one to control the assembling step are also appearing (Fig. 3). This combination between the "nanobuilding block approach" and "templated assembling" will have paramount importance in exploring the theme of "synthesis with construction". Indeed, they exhibit a large variety of interfaces between the organic and the inorganic components (covalent bonding, complexation, electrostatic interactions, *etc.*). These NBB with tunable functionalities can, through molecular recognition processes, permit the development of a new vectorial chemistry.[38,39]

Path D *Integrative synthesis* (lower part of Fig. 3). The strategies reported above mainly offer the controlled design and assembling of hybrid materials in the 1 Å to 500 Å range. Recently, micro-molding methods have been developed, in which the use of controlled phase separation phenomena, emulsion droplets, latex beads, bacterial threads, colloidal templates or organogelators leads to controlling the shapes of complex objects in the micron scale.[30,34] The combination between these strategies and those above described along paths A, B, and C allow the construction of hierarchically organized materials in terms of structure and functions.[30,34] These synthesis procedures are inspired by those observed in natural systems for some hundreds of millions of years. Learning the "*savoir faire*" of hybrid living systems and organisms from understanding their rules and transcription modes could enable us to design and build ever more challenging and sophisticated novel hybrid materials.[1,2,30,34,40,41]

III. Applications of hybrids

Commercial applications of sol–gel technology preceded the formal recognition of this technology. Likewise, successful commercial inorganic–organic hybrids have been part of manufacturing technology since the 1950s. As Arkles pointed out in a previous work,[14] a "commercial product" is the one that is both *offered for sale* and *used* in the regular production of a device or item in general commerce. In this section numerous examples of "commercial" as well as "potentially commercial" hybrid materials will be illustrated.

III.1. Possible synergy between inorganic and organic components

For a long time the properties of inorganic materials (metals, ceramics, glasses, *etc.*) and organic compounds (polymers, *etc.*) shaped as bulks, fibers or coatings have been investigated with regard to their applications, promoting the evolution of civilizations. During the last fifty years with the help of new analysis techniques and spectroscopic methods the structure/properties relationships of these materials became clearer and their general properties, tendencies and performances are well known. Some of these general properties are summarized in Table 1.

The choice of the polymers is usually guided mainly by their mechanical and thermal behavior. But, other properties such as hydrophobic/hydrophilic balance, chemical stability, bio-compatibility, optical and/or electronic properties and

Table 1 Comparison of properties of conventional organic and inorganic components[8f]

Properties	Organics (polymers)	Inorganics (SiO_2, TMO)
Nature of bonds	covalent [C–C] (+ weaker van der Waals or H bonding)	ionic or iono-covalent [M–O]
T_g (glass transition)	low (−100 °C to 200 °C)	high (>200 °C)
Thermal stability	low (<350 °C, except polyimides, 450 °C)	high ($\gg$100 °C)
Density	0.9–1.2	2.0–4.0
Refractive index	1.2–1.6	1.15–2.7
Mechanical properties	elasticity	hardness
	plasticity	strength
	rubbery (depending on T_g)	fragility
Hydrophobicity, permeability	hydrophilic	hydrophilic
	hydrophobic	low permeability to gases
	± permeable to gases	
Electronic properties	insulating to conductive	insulating to semiconductors (SiO_2, TMO)
	redox properties	redox properties (TMO)
		magnetic properties
Processability	high:	low for powders (needs to be mixed with polymers or dispersed in solutions)
	• molding, casting	
	• machining	
	• thin films from solution	high for sol–gel coatings (similar to polymers)
	• control of the viscosity	

chemical functionalities (*i.e.* solvation, wettability, templating effect, *etc.*) have to be considered in the choice of the organic component. The organic in many cases allows also easy shaping and better processing of the materials. The inorganic components provide mechanical and thermal stability, but also new functionalities that depend on the chemical nature, the structure, the size, and crystallinity of the inorganic phase (silica, transition metal oxides, metallic phosphates, nanoclays, nanometals, metal chalcogenides). Indeed, the inorganic component can implement or improve electronic, magnetic and redox properties, density, refraction index, *etc.*

The wide choice of synthetic procedures for obtaining organic–inorganic structures (see section II) preludes the vast range of properties which could be reached by these materials. Obviously, the final materials are not only the sum of the primary components and a large synergy effect is expected from the close coexistence of the two phases through size domain effects and nature of the interfaces. Then, searching for a material with a given property could appear as an endless play. Hopefully, in the past twenty years guidelines have been drawn out from the basics of material, sol–gel and polymer sciences. Generally, the major features of each phase are preserved or even improved in the hybrid materials (stability, thermal behavior, specific properties, *etc.*), and furthermore, new properties coming from the synergy of both components are commonly observed as well.

For example, there is a widespread agreement in the scientific community that active optical applications of hybrid nanocomposites might present a very attractive field to realise applications for the 21st century. Indeed, the exploitation of active optical properties of photoactive coatings and systems is strongly emerging. In particular, hybrid materials having excellent laser efficiency and good photostability,[42,43] very fast photochromic response,[44] very high and stable second order non-linear optical response,[45] or being original pH sensors,[46] electroluminescent diodes[47] or hybrid liquid crystals[48] have been reported in the past years. Many of these promising functional hybrid materials have significant commercial potential but they have not yet achieved commercial status.

Therefore, in the following sections we will describe some striking examples of hybrid materials with emerging potentialities, as well as functional hybrids with real applications, selecting them among commercially available hybrids and existing prototypes very close to the market.

III.2. Hybrids obtained *via* encapsulation of organics in sol–gel derived matrices

Organics molecules, oligomers, macromonomers and biocomponents can be easily incorporated into metal oxide-based networks or hybrid siloxane–oxide matrices by mixing them with metal alkoxides or/and organosilanes in a common solvent. In this case, organic components get trapped during hydrolysis and condensation reactions, according to path A1 of Fig. 3. However, organic components can also be introduced by impregnating them inside the porous network.[49] Both strategies have been extensively developed either by inorganic sol–gel chemists or by polymer chemists. The host matrix can be made of an inorganic structure (silica, titania, *etc.*) or a hybrid skeleton (siloxane–metal oxide hybrids, organosilicas, *etc.*). These amorphous composites exhibit a wide variety of interesting properties (mechanical, optical, electrical, ionic, sensors, bio-sensors, catalysts, *etc.*) which may be improved *via* the control of their microstructure.

III.2.a. Organic molecules (dyes and "active species") in amorphous sol–gel matrices. Organic molecules play an important role in the development of optical systems: luminescent solar concentrators, dye lasers, sensors, photochromic, NLO and photovoltaic devices. However, the thermal instability of these compounds has precluded their incorporation into inorganic oxide matrices till the use of sol–gel derived glasses by Avnir, Levy and Reisfeld.[49–51] Since then, many organic dyes such as rhodamines, pyranines, spyrooxazines, chromenes, diarylethenes, coumarins, NLO dyes, *etc.* have been incorporated into silica or aluminosilicate based matrices, giving transparent films or monoliths with good mechanical integrity and excellent optical quality, as illustrated in Fig. 4.[52]

Nowadays, abundant sol–gel derived hybrid materials yield easy-to-process materials that offer many advantages such as tunable physical properties, high photochemical and thermal stabilities, chemical inertness and negligible swelling in both aqueous and organic solvents. Some striking examples based on the optical properties of hybrids concern:

(i) "Silica–organic chromophore–surfactant" pH sensitive hybrid composites in a wide acido-basic range.[46] Indeed, the co-entrapment in silica based monoliths of the surfactants with an extensive series of pH indicators greatly modifies the indicating performance of the pH probe; it leads to much larger pK_i shifts, but also greatly improves the leaching profiles with half lives ranging from several months to several years. Moreover, the organic template stabilizes the microscopic structure of the material upon heat-drying; this provides a potential solution to the problem of structural changes inherent to sol–gel materials long after the completion of their synthesis.

(ii) Photochromic materials designed from spyrooxazines embedded in hybrid matrices that give very fast optical responses depending on the tuning of dye–matrix interaction.[52]

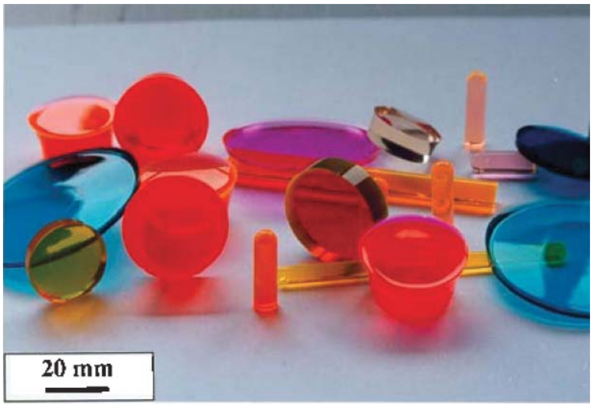


Fig. 4 Hybrid organic–inorganic materials containing organic chromophores (courtesy of Dr Chaput, École Polytechnique, Palaiseau).

This implies a perfect adjustment of the hydrophilic–hydrophobic balance and of the rheo-mechanical properties.[48,53,54] Such novel materials can be synthesized either from co-condensation between $MeHSi(OR)_2$ and $HSi(OR)_3$ reactive precursors[44] or from telechelic $[\alpha\text{–}\omega(COO)PEG]^{2-}$ chains connected by $[(BuSn)_{12}O_{14}(HO)_6]^{2+}$ tin-oxo clusters.[53] Both hybrid matrices are flexible and can incorporate large amounts of photochromic dyes in soft aprotic domains allowing intense and fast optical responses.

(iii) Hybrid materials built from organically modified silicas by NLO chromophores exhibiting very high second order optical non-linearity.[45] The achievement of these materials is related to the quadratic susceptibility of the dye and the thermal stability of the hybrid matrix. Second order non-linearities are only observed after poling the materials in order to induce anisotropic orientations of the organic dyes. Inorganic–organic hybrid matrices, obtained from hydrolysis and condensation of a siloxane precursor bearing azo-dyes and $Si(OMe)_4$, exhibit high non-linearities analogous to those reported for inorganic solids and organic polymeric materials. Grafting of the dye allows the incorporation of a high concentration of chromophores and inhibits possible dye motional relaxations after poling and cross-linking. On the other hand, the silica component yields a better optical quality and increases the matrix rigidity also prone to maintain the induced anisotropy. This strategy permitted the tuning of large non-linearities (d_{33} = 150 pm V^{-1} at 1.34 μm) and the conservation of its stability at room temperature or at higher temperatures (80 °C).

(iv) Several drastic conditions are required to elaborate efficient solid-state organic dye lasers. Indeed the laser material must exhibit excellent transparency without scattering, well-polished surface, good slope efficiency, high output-energy pumping, sufficient thermal conductivity, long lifetime, and stability to aging. These exigencies can be achieved in hybrid materials by optimizing the dye/matrix system.[3,5] Indeed, the optimization of hybrid solid-state dye-laser materials containing stable and efficient dyes such as perylenes and pyrromethenes yields a set of very promising materials that must be able to enter the market. Their performances such as slope efficiency of more than 80%, maximum output energies reaching a few mJ, lifetimes of more than 10^6 pulses in the mJ range improved a lot over the past few years. In particular, the elaboration of a stable pyrromethene derivative-doped hybrid material with a huge lifetime of 5×10^5 pulses (2×10^6 pulses by removing oxygen from the same sample) at 1 mJ with a repetition rate of 20 Hz which exhibits a good laser emission in the 550–650 nm range was achieved by Canva *et al.*[43] It is now clear that this efficiency, the tunability range (up to 60 nm) and the spatial beam quality are similar to those obtained in equivalent liquid solutions. Experiments with hybrid solid-state organic dye lasers were also performed in a configuration for which the sample was continuously moved indicating that the laser system can operate at about 1 mJ output energy at 20 Hz with a single sample for several months. These results are very promising and it may be forecast that effective tunable solid state dye lasers will replace liquid dye laser systems in certain applications.[52]

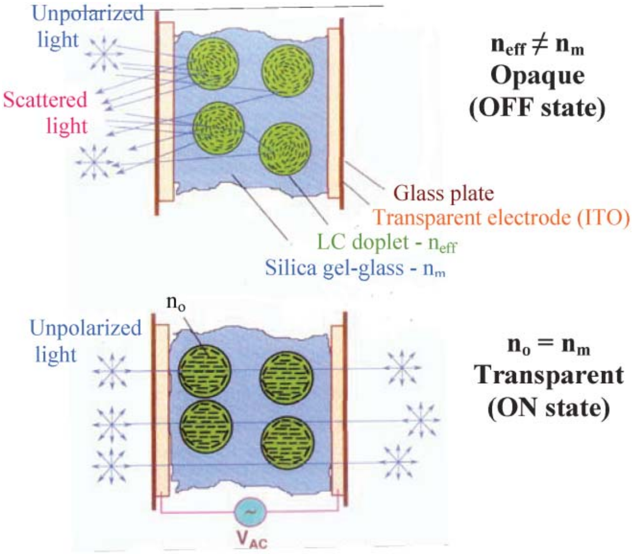


Fig. 5 Encapsulation of liquid crystal microdroplets in a sol–gel thin film: Illustration of the optical shutter mechanism.[48,55]

(v) New electro-optical devices constituted of organic nematic liquid crystal dispersed into sol–gel glasses are very promising.[48,55] As the liquid crystal micro-droplets scatter visible light, the hybrid material remains white or opaque. If 20–60 mm of this material is sandwiched between transparent electrodes (Glass Dispersed Liquid Crystals coined GDLC by David Levy), upon application of a voltage, the hybrid can switch from opaque to clear, forming therefore a light shutter. When the voltage is removed, the LC droplets return to their original scattering orientation. Fig. 5 schematizes the constituents and mechanism of this optical shutter.

Embedding in sol–gel glasses provides a convenient way to protect the liquid crystal from physical damage (humidity, evacuation of LC outside the cell, *etc.*). In this way, no hermetic sealing is needed, extending the range of applications to large displays with a higher stability, without increasing their cost per surface unit. Moreover, in the future, GDLC will likely pass beyond the prototype step and enter the market of devices for visual presentation because GDLC based coloured displays can also be easily obtained by incorporating organic dyes in the hybrid material either in the sol–gel matrix or in the liquid crystal phase itself.

All these hybrid materials and systems are coming out of the labs and increasingly entering into our daily life. Indeed, some of these hybrid products have already entered the applied field and the market. Concerning direct applications of photochromic based hybrids Protavic SG FP has successfully embedded a high concentration of photochromic dyes in sol–gel derived hybrid materials by tailoring the dye–matrix interactions. Thus, Protavic has commercialized photochromic varnishes from which thin films exhibiting a high optical contrast and a drastically reduced time for coloration–decoloration cycles can be easily processed.[56,57] Another approach consists of elaboration of efficient photochromic hybrids by means of thermally cured hybrid polymers which contain photochromophores covalently attached (class II hybrids) to the inorganic silica based backbone.[52,58–61]

Depending on the nature of the photochromic dye (spyrooxazine, diarylethene, *etc.*) such materials can be used as fast switches, for writing channel waveguides or for optical data storage.

In terms of larger industrial markets, Essilor processes scratch-resistant coatings based on siloxane hybrid resins deposited on polymeric lenses. Dye-containing hybrid materials are also hiding in the screens of the one million TV sets sold annually by Toshiba.[62] Such screens are coated with a sol–gel material made of indigo dye embedded in a silica/zirconia matrix.[62] Interestingly, this 21st century advanced hybrid material brings us strong echoes of ancient Maya Blue.

The use of embedded organic molecules (such as chomophores) in silica based host matrices was pioneered by Avnir and collegues.[49] A similar strategy was used to develop a set of class I hybrids compounds by Sol–Gel technologies, some of which are sold by Merck KgaA and EMD Chemicals Inc.[63]

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.[64,65] They are based on the encapsulation of active organic components within more or less porous silica micro-capsules.

Undesirable skin alterations and melanomas created by sun induced premature skin aging need the use of efficient but biocompatible sunscreens. Nowadays, commercial sunscreens are directly applied to the skin and usually contain an extremely high amount of active ingredients. This can be detrimental to health when they are adsorbed by skin and they are not photostable, thus generating free radicals that may cause damage to the DNA.

The hybrid materials developed by Sol–Gel technologies answered to these points. Indeed, by encapsulating the active organic UV filters (80% w/w of the final product) in silica micro-capsules the contact of these potent chemicals with the skin is reduced, and damage from free radicals that may get trapped within the porous host is prevented.

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, as shown in Fig. 6.

The same company has also developed silica rainbow pearls containing organic dyes for cosmetics applications and silica active-pearls containing an effective acne medication such as benzoyl peroxide, which are as effective as antibiotics but do not causes bacterial resistance or stomach upset. Benzoyl peroxide in direct contact with skin provokes skin irritation, 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 the epidermis while gradually delivering it into the follicular region where acne bacteria are found.

III.2.b. Bioactive sol–gel derived hybrid materials. Bioactive hybrids find applications in the field of biotechnology for the realization of biosensors and bioreactors. These fields have been recently reviewed by Livage *et al.*[66] They take advantage of the high activity of enzymes, antibodies or micro-organisms to perform specific reactions that would not be possible with the usual chemical routes. Active biospecies are immobilized on or in solid substrates in order to be reusable and protect them from denaturation. Natural and synthetic polymers (polysaccharides, polyacrylamides, alginates, *etc.*) are currently used for bio-immobilization *via* covalent binding or entrapment. However inorganic materials such as sol–gel processed glasses and ceramics offer significant advantages over organic polymer hosts. They exhibit better mechanical strength together with improved chemical and thermal stability. Moreover they don't swell in most solvents preventing the leaching of entrapped bio-molecules.

Enzymes are biological catalysts responsible for the chemical reactions in living organisms. Their high specificity and huge catalytic power are due to the fact that the geometry of the active site can fit exactly that of the substrate. Many biocatalysts such as enzymes or catalytic antibodies are available for performing a variety of synthetically important transformations or for bio-sensing applications.

A large number of enzymes have already been trapped within sol–gel matrices but glucose oxidase (GOD) is by far the most studied enzyme. It is known to catalyze the oxidation of glucose by molecular oxygen and finds many applications in clinical analysis for the diagnosis of diabetes and in the food industry. Optical bio-sensors or amperometric biosensors have been extensively used in biosensors for the titration of glucose.[67] A new kind of hybrid biosensor based on changes in enthalpy during the enzymatic oxidation of glucose recorded as a thermometric peak by a sensitive thermistor has been recently described in order to detect glucose in fruit juice, Coca Cola and human blood serum.[68]

Another example of importance is the catalytic activity of lipases in organic solvents. Normally these enzymes catalyze

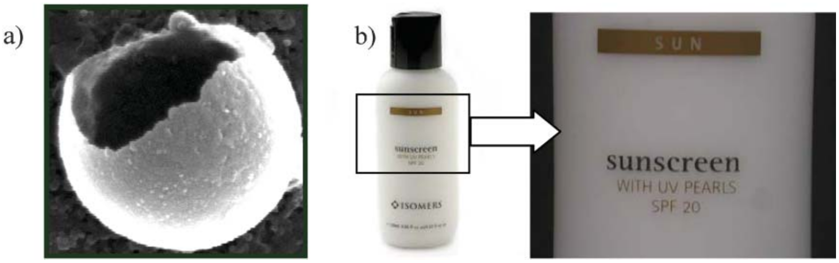


Fig. 6 (a) Micrograph of a core–shell capsule for carrying functional contents. (b) Commercial Isomers Sunscreen SPF 20 with UV Pearls.[63]

the hydrolysis of esters with formation of carboxylic acids and alcohol. Since an excess of water is present the reverse esterification reaction which is the actual synthetic target cannot be achieved. However the use of lipases in suspension in an organic solvent makes possible chemio-selective, regio-selective and stereo-selective esterification or transesterification. Most lipases are quite robust however their use as industrial catalysts is slow because enzyme activity in organic solvents is rather low, the long term stability is limited, the separation of lipase from the products in some cases is difficult and reuse of the catalyst yields some problems. In order to solve these problems of stability and recyclability immobilisation of enzymes is the most obvious strategy. Ease of performance, increase enzyme activity and long term ability are not trivial goals and generally studies reported on enzyme immobilisation only achieve one of these performances. An alternative and interesting approach concerns the encapsulation of enzymes in sol–gel derived matrices. Reetz developed a successful sol–gel procedure strategy:[69] he carried out the entrapment of lipases in hydrophobic hybrid organic–inorganic matrices obtained through hydrolysis and co-condensation of R–Si(OR)$_3$ and TEOS. The resulting new class of heterogeneous bio–organic–inorganic hybrid catalysts display very high catalytic activities with immediate applications in chemo-selective, regio-selective and stereo-selective organic transformations. In this sense, Fluka already commercializes some promising candidates in the areas of fine chemicals and pharmaceuticals as well as in the derivatization and refining of fats and oils.

Other applications of bio-hybrids are emerging. Antibody-based affinity biosensors have been used for the detection of various chemicals such as fluorescein,[70] dinitrobenzene (DNB)[71] or dinitrophenyl (DNP).[72] Hybrid sol–gel immunosensors have been developed for the analysis of pesticides.[73]

Immobilization of cells appears also to be an important challenge for biotechnology. Their metabolic activity can be used in a large variety of processes for food industry, waste treatment, production of chemicals or drugs and even cell transplantation. In particular the bio-compatibility of silica gels and their high porosity favouring water retention and nutrient diffusion make them interesting hosts for the culture of bacteria[74] or fungi.[75]

Antibodies trapped within sol–gel matrices allow the construction of efficient immunoaffinity devices or for medical applications to make blood tests. Livage *et al.*[76,77] developed new bio-hybrid matrices using *Leishmania donovani infantum* promastigotes as antigens trapped within silica gel. These bio-hybrids were used to detect the presence of specific antibodies in the serum of human and dogs through the so-called ELISA (Enzyme Linked ImmunoSorbent Assays) tests.

Cell transplantation is also a promising technique in order to avoid the usual organ transplantation. However foreign cells have to fight against immune rejection. Therefore, the encapsulation of living cells within porous membranes represents a good alternative to shield the cells from immune attack. Several articles have recently described the encapsulation of single cells or cell aggregates within silica capsules or alginate microspheres coated by a silica layer.[78,79]

Encapsulated cells such as Langerhans islets involved in the metabolism of glucose and the production of insulin are under study at ‘‘Solgene Therapeutics LLC’’ in USA.[80]

The ‘‘biosil’’ process based on the encapsulation of swine hepatocytes and rat liver deposited onto a substrate and then partially covered by a silica film *via* the gas phase is used for extracorporeal bioartificial organs. Theses bio-hybrids have already been used as a bridge to liver transplantation in patients with fulminant hepatic failure.[81] Biogel transplants could emerge as a useful treatment for diseases such as diabetes.

Indeed, the scientific investigations performed by different groups (Livage, in France, Avnir in Israel, Dunn in USA, Carturan in Italy) demonstrate that sol–gel encapsulation of bio-components offers an easy and generic immobilization procedure that could compete with usual encapsulation processes. Few hybrid bio-catalysts and hybrid bio-sensors are already in the market or very close to development. The future of these sol–gel derived bio-hybrids might be related to the fields of bio-medical applications. In that case, preserving the viability of cells within sol–gel derived hybrid matrices appears to be a real challenge. Recent studies indicating that encapsulated bacteria (*E. coli*) can survive the gelation procedure and remain able to continue normal metabolic activity within the gel matrix are very promising.[82]

Looking to the future, the control of the morphology, from the nano to the micrometer scales, associated with the incorporation of several functionalities, with a perfect control of concentrations and spatial dispersions, can yield entirely new hybrid materials with not only original and complex architectures but also optimized properties and various roles.[1,30] The design and processing of innovative materials coupling original diagnostic and/or therapeutic properties such as magnetic resonance imaging (MRI) contrast, hyperthermia, radioactivity, safe transport and drugs controlled release are in progress (‘‘FAME’’ network of excellence).

III.2.c. Biomaterials and bio-inspired hybrid constructions. Natural materials offer remarkable hydrodynamic, aerodynamic, wetting and adhesive properties. Evident interesting applications concern surface coatings with anti-fouling, hydrophobic, protective or adhesive characteristics and also cosmetic products.

One way to take advantage of the emerging field of biomimetics is to select ideas and inventive principles from nature and apply them in engineering products.[1] Materials reproducing structures described in animals and plants already exist: ‘‘Riblets’’ are plastic films covered by microscopic grooves inspired by shark or dolphin skin that are placed on airplane wings in order to reduce the hydrodynamic trail and economize fuel;[83] Nylon or Kevlar were inspired from natural silk and Velcro was inspired by the hooked seed of goosegrass.[84–86] Concerning hybrid materials, a known example concerns super hydrophobic or super hydrophilic coatings[87] inspired by the microstructure of lily leaves. Indeed, combining controlled surface roughness of an inorganic (glass, for example) or organic substrate in the micron-scale with hybrid layers obtained by polycondensation of hydrophobic organo-silanes yields transparent coatings with exalted

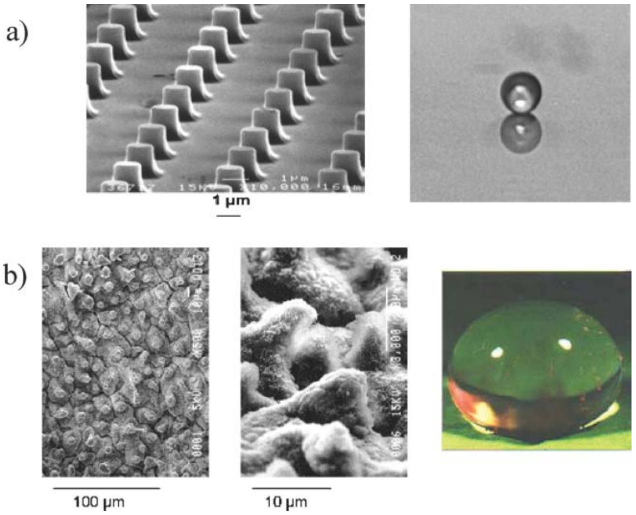


Fig. 7 Artificial super hydrophobic coatings (a) inspired by lily leaves (b).

hydrophobic behaviour (exhibiting wetting angles much greater than 120°, see Fig. 7).

The research concerning materials for implants or prosthesis includes all materials or systems for clinical applications to replace part of a living system or to function in intimate contact with living tissues. Hybridization of materials or implants by bioactive molecules will help specific cells to interact with the surrounding matrix and to perform recognition, adhesion, migration, proliferation and remodelling.[1,88,89] The role of these "bio-coupling molecules" will be for example to promote new tissue formation and degrade the implanted material by specific enzymes.

In living systems, many biomineralization processes involve the migration of a front line of mineral domains through the organic matrix. However, this process is carefully controlled by using sets of diversified sensors. In biotechnology, techniques such as stereolithography, multilayering and three-dimensional printing seem to be very promising since they allow the formation of new hybrid nanocomposites shaped as films or bulk through approaches similar to those of nature.[90–92] Growth by successive layer deposition offers better control of the material's resulting properties together with the incorporation of sensors which could perform non-destructive tests at different fabrication steps as a function of size, volume or aging. In the long term, objects for domestic use, evolutionary bio-hybrid implants and biomaterials showing better biocompatibility should appear. These approaches could not only allow the achievement of three-dimensional innovative hybrid nano-composites but also "smart" materials such as bio-cements controlled over time with the capacity to self-repair.[1,90–92]

III.3. Class II hybrids: ORMOCER®s as an example of highly tuneable functional hybrids

In this section, some general remarks about the synthesis of class II sol–gel hybrid materials, as well as some of the most striking examples of hybrids with real applications, will be shown. It must be noticed that materials scientists have learned to create smart hybrid materials exhibiting exceptional properties, as a result of the possibility to combine different properties such as transparency, good adhesion, barrier effect and corrosion protection, easy tuning of the refractive index, adjustable mechanical properties, decorative properties, functional properties (absorption, luminescence, NLO or sensing), *etc.* in a unique material.

III.3.a. General chemistry of hybrid ORMOCER®s. The strategy to construct class II hybrid materials consists of making intentionally strong bonds (covalent or iono-covalent) between the organic and inorganic components. Organically modified metal alkoxides are hybrid molecular precursors that can be used for this purpose.[93] The chemistry of hybrid organic–inorganic networks is mainly developed around silicon containing materials. Currently, the most common way to introduce an organic group into an inorganic silica network is to use organo-alkoxysilane molecular precursors or oligomers of general formula $R'_nSi(OR)_{4-n}$ or $(OR)_{4-n}Si–R''–Si(OR)_{4-n}$ with n = 1,2,3.

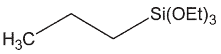
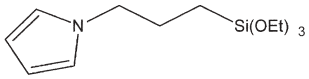
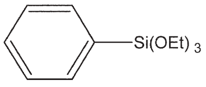
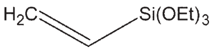
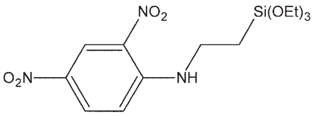
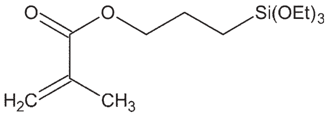
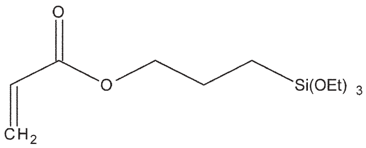
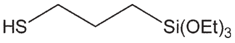
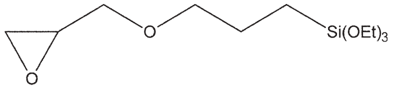
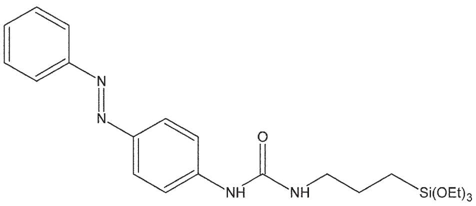
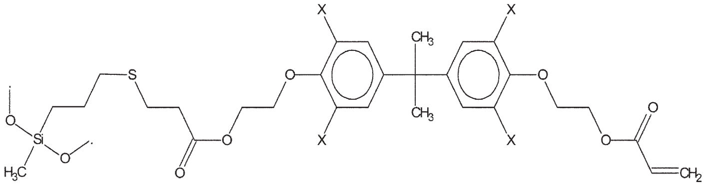
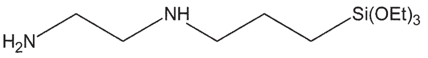
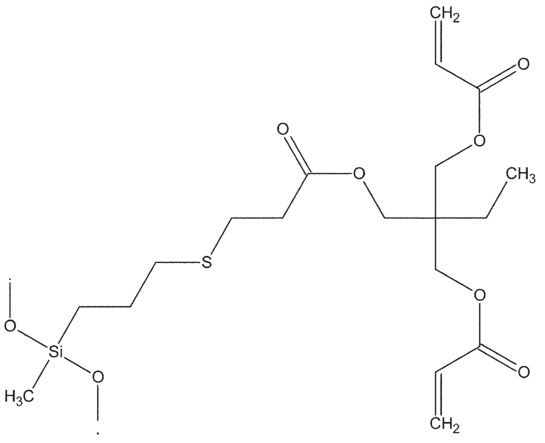
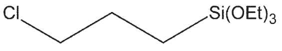
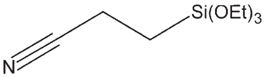
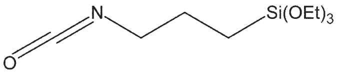
In most sol–gel conditions the Si–C bond remains stable towards hydrolysis and the R′ group introduces focused new properties to the inorganic network (flexibility, hydrophobicity, refractive index modification, optical response, *etc.*).

Organic groups R′ can be introduced into an inorganic network in two different ways: as network modifiers or network formers. Both functions have been achieved in the so-called ORMOCER®s (registered trademark of Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e. V. in Germany). Since the eighties, they have been extensively studied and developed by the Fraunhofer Institut für Silicatforschung, Würzburg.[93–99] The organic group R′ can be any organofunctional group. If R′ is a simple non-hydrolyzable organic group ($Si–CH_3$, Si–phenyl, *etc.*) it will have a network modifying effect. Moreover if R′ can react with itself (R′ contains a vinyl, a methacryl or an epoxy group for example) or additional polymerisable monomers, it acts as a network former. Some examples of network formers and network modifiers are gathered in Table 2. Polymeric components can also be introduced in hybrid nanocomposites by using functionalised macromonomers (R″) of general formula $(OR)_{4-n}Si–R''–Si(OR)_{4-n}$ with n = 1,2,3. Some examples of these trialkoxysilyl functionalised polymers are gathered in Table 3.

The sol–gel synthesis of siloxane based hybrid organic–inorganic compounds usually involves di- or trifunctional organosilanes co-condensed with metal alkoxides, mainly $Si(OR)_4$, $Ti(OR)_4$, $Zr(OR)_4$ or $Al(OR)_3$. Each of these components has specific roles that have been reviewed and discussed extensively.[100]

Trifunctional alkoxysilanes and metal alkoxides are efficient crosslinkers that usually lead after co-condensation to hybrid materials having high Young's modulus ($E > 10$ GPa) and either high glass transition temperature ($T_g >$ RT) or no T_g. Difunctional alkoxysilane co-condensed metal alkoxides generate linear polymers and cyclic oligomers that behave as hybrid elastomers and exhibit low Young's modulus (E = 5–100 MPa) and low glass transition temperature ($T_g <$ RT). Therefore, mixing these different molecular precursors

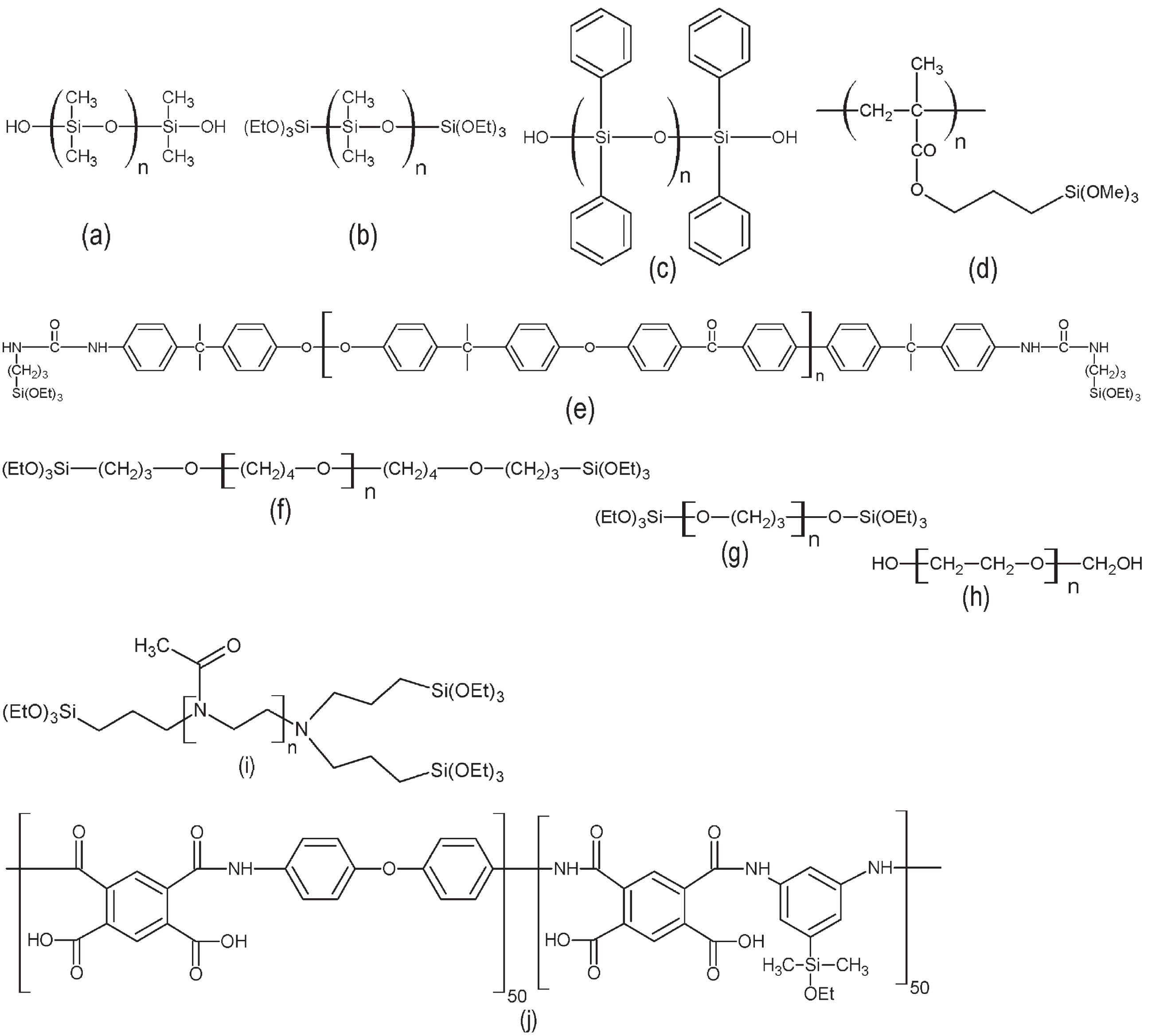
Table 2 Examples of network formers and network modifiers

Network modifiers	Network formers
Methyltriethoxysilane H_3C–$Si(OEt)_3$ Propyltriethoxysilane 	Metal alkoxides $Al(OEt)_3$, $M(OEt)_4$ with M = Ti, Zr *N*-(3-Triethoxysilylpropyl)pyrrole 
Phenyltriethoxysilane 	Vinyltriethoxysilane 
3-(2,4-Dinitrophenylamino)propyltriethoxysilane 	Methacryloxypropyltriethoxysilane 
Aminopropyltriethoxysilane 	3-(Trimethoxysilyl)propylacrylate 
Mercaptopropyltriethoxysilane 	3-(Glycidoxypropyl)triethoxysilane 
4-(3-Triethoxysilylpropylureido)azobenzene 	
3-(2-Aminoethylamino)propyltriethoxysilane 	
3-Chloropropyltriethoxysilane 	
2-Cyanoethyltriethoxysilane 	
Isocyanatopropyltriethoxysilane 	

(tri- and di-functional alkoxysilanes, metal alkoxides, functional macromonomers, *etc.*) allow mechanical and functional properties of hybrid materials to be tuned between those of polymers and glasses.

For example the microstructure of the resulting hybrids, ORMOCER®s, can be strongly modified by using trifunctional silicon alkoxide $R'Si(OR)_3$ in which R′ is a polymerisable organic group such as vinyl, epoxy or methacrylate. Patternable coatings have been prepared from sols obtained by co-condensing TEOS, metal alkoxides and organosilane precursors such as γ-glycidyloxypropyl trimethoxysilane, γ-methacryloxypropyl trimethoxysilane or

Table 3 Structure of some functionalized macromonomers used in sol–gel synthesis of hybrid materials: (a) hydroxyl-terminated polydimethylsiloxane, (b) triethoxysilyl-terminated polydimethylsiloxane, (c) hydroxyl-terminated phenylsilsesquioxane, (d) trimethoxysilyl-functionalized, (e) triethoxysilyl-terminated poly(arylene ether) ketone, (f) triethoxysilyl-terminated poly(tetramethylene oxide), (g) triethoxysilyl-terminated poly(oxypropylene), (h) polyethyleneglycol, (i) triethoxysilyl-terminated polyoxazoline, (j) ethoxysilyl-functionalized polyimide



vinyl trimethoxysilane. Organic polymerisation is then induced by photochemical or thermal curing. Patterning can be realized by photolithographic methods or even by direct laser writing.[100]

The synthesis and processing of hybrid contact lenses provides a nice example of the versatile tailoring permitted by hybrid materials chemistry. A ''silicon''-like unit, having a –Si–CH$_2$–CH$_2$– group was chosen to favour oxygen diffusion, while a CH$_2$OH group was considered to be suitable for hydrophobicity. However the combination of these functional silanes in a sol–gel process leads to back esterification reactions of the –Si(CH$_2$)$_n$OH to the Si–R group by destroying the hydrophilic –CH$_2$OH groups. Therefore a –Si(CH$_2$)$_n$-epoxy group was chosen and the ring opening was performed after hydrolysis and condensation of the alkoxy groups. The resulting hybrid material exhibits good oxygen permeation and hydrophobicity but a porous texture and poor mechanical properties. Ti(OR)$_4$ was then added as a condensation catalyst leading to dense but brittle materials which were not suitable for lenses. Consequently, –Si(CH$_2$)$_n$–O–CO–CH(CH$_3$)=CH$_2$ was introduced and copolymerized with MMA (methyl methacrylate). Mechanical properties were sufficient but wettability was drastically decreased. The wettability came back when MMA was substituted by HEMA (hydroxyl methyl methacrylate). The resulting material exhibited all required properties but the unexpected part was that it showed a better scratch resistance.[97]

Another interesting discovery was that hybrids made from PDMS and TEOS could be rubbery even when the inorganic component weight was in excess of 70%. These rubbery hybrids materials[101–103] exhibited properties comparable to

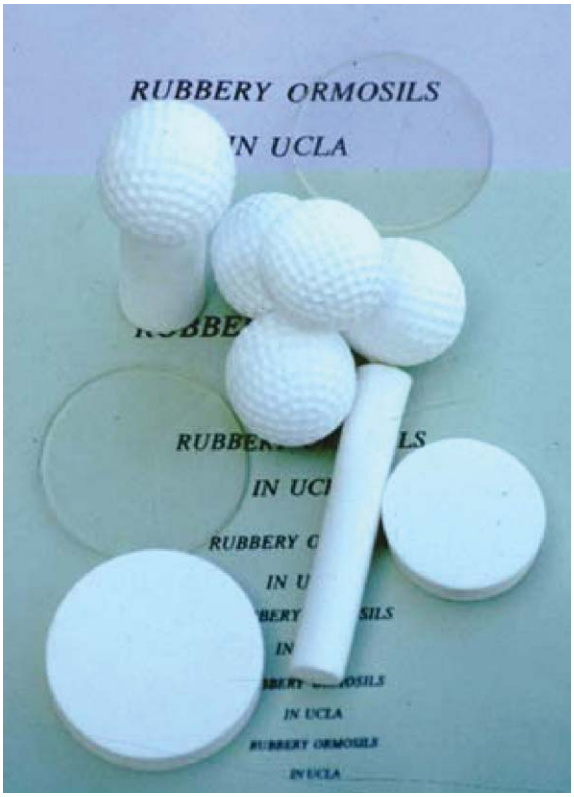


Fig. 8 Rubbery hybrids with different shapes. Courtesy of E. Bescher and J. D. Mackenzie.[103,104]

those of organic rubbers. The more rubbery hybrid was synthesized with a much higher acid concentration (H^+/Si = O.3). The strong acidity of the medium increases the hydrolysis rates of Si–OR species rapidly providing silanol groups but slows down condensation reactions providing small silica polymers and it also modifies the distribution of the species contained in the commercial PDMS polymers. The removal by evaporation of cyclic species may lead to an increase of the matrix porosity. The resulting material consist of a matrix of medium chain length and small silica particles with a porous structure. This porous texture produces free volume needed for chain motion. As a consequence, the PDMS chains can curl and uncurl in the presence of external stress and the material exhibits rubbery elasticity.

Furthermore, these rubbery hybrids can be specifically shaped, giving objects such as those illustrated in Fig. 8.

Extensive investigations have been also performed about organically derived silica-based materials obtained through surface grafting reactions for other key applications such as gas chromatography[105–108] and membranes.[109]

III.3.b. Hybrid materials for protective and decorative coatings[110–118].

One of the earlier examples of commercial hybrids with protective functions can be found in the painting industry. In fact, zinc-based sol–gel inorganic paints were and are still employed as corrosion-resistant primers and high-temperature coatings for steel.[119] However, from the 1950s, the intense study developed on organically modified silane precursors led to resin formulations within the range of high-performance weather-resistant coatings. Thus, functional alkoxysilsesquioxane copolymers can be used on superstructures for naval aircraft (phenylsilsesquioxanes),[120] in coil coating applications (silsesquioxane–polyester mixtures)[121] or as release resins for baking pans and utensils (compositions incorporating difunctional alkoxysilanes).[122]

Hybrid ORMOCER® coatings are even developed to strengthen parts of paper, to enhance specific properties of polymers used in industry (polyethylene, cellulose, *etc.*) or to reduce the abrasion of leather, when used *e.g.* in handbags. In this sense, chemical interactions between titanium alkoxides and cellulose or proteins have been reported since a long time ago,[123] and their industrial applications led to the registration of numerous patents (quick-drying varnishes, coatings from fatty acid esters of epoxy resins, cellulose, *etc.* with organotitanium precurors).[124] Silicon and titanium–organic precursors have been used as additives in polyamide-based inks involved in the polyethylene impression/dyeing process in order to enhance the ink–polymer substrate adherence, to ease the homogenization of the different constituents, and to improve thermal, solvent and humidity resistance.[125] The cross-linking action in these functionalized polymers is reached thanks to hydrolysis and condensation reactions of their reactive hydroxyl groups with the metal-oxo precursors.

Likewise, involving scratch and abrasion resistance applications, numerous ORMOCER® based coating materials for sensitive surfaces have been on the market since the 1980s. In general, these protective materials are based on epoxy functionalized alkoxysilanes polycondensed with Al, Ti or Zr compounds. Depending on the content and choice of heteroatoms the hard-elastic material shows more or less resistance (it decreases in the following order Zr > Ti > Al); however, their content must be limited according to the brittleness of the coating. Once the polycondensed material is prepared, it is diluted in a specific solvent and deposited on the sensitive substrate by dipping, spraying or spin-on application, followed by a later UV and/or thermal curing.

The composition and functionality of the systems strongly vary according to the substrate material (special optical polymer like CR39, PMMA, polycarbonate, *etc.*) to be coated as they demand different curing conditions, adapted physical properties and characteristics (antisoiling, antistatic or diffusion-inhibiting properties)[126] as well as functionality for better wetting and adhesion. Dyes, pigments and fillers may also be added for specific applications, leading to smart multifunctional hybrid coatings.

Some interesting examples of protective ORMOCER® coatings are provided by T_O_P GmbH, who produce lacquers developed by the Fraunhofer ISC.[127–130] In fact, lacquer synthesis facility enables a large scale production of coating materials like ABRASIL®, CLEANOSIL® and DEKOSIL®. All these lacquers are colourless and highly transparent, which make them highly suitable for the ophthalmic market. Fig. 9a shows a plate half coated with ABRASIL® and how the scratch traces from steel wool are observed on the uncoated half. This high scratch resistance is achieved with layer thicknesses of only a few micrometers. Fig. 9b shows an injection moulded plastic part coated with ABRASIL®. After coating and an adequate UV curing,

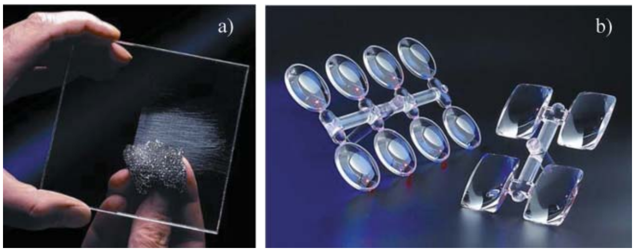


Fig. 9 Two examples of protective ORMOCER® coatings: (a) plate half coated with ABRASIL®; (b) injection moulded (plastic) part coated with ABRASIL® and UV cured.[127–130]

handles are attached to make magnifying lenses for every day use.

An interesting and highly productive application of inorganic–organic hybrid materials is in automotive coatings. In this technology, hybrid coatings that provide not only coloration but also scratch-resistance and protection from environmental factors such as UV and chemical attack are required. These conditions were firstly accomplished by Dupont with Generation 4®, which consist of a complex mixture of two hybrid polymers cross-linked simultaneously during curing to form a polymer network that is partially grafted and partially interpenetrated.[131] This hybrid consists of a high-density acrylate polymer core, organically modified with alkoxysilane groups and residual unsaturations, which confers a high-modulus and scratch-resistant function, dispersed in a low cross-linked density polymer, which provides film-forming properties. The superior scratch and environmental-etch resistance of these hybrid coatings led to their acceptance as topcoats for eight of the ten top-selling automobiles for 1997, including the Ford Taurus, Toyota Camry, and Honda Civic/Del Sol.

Decorative hybrid coatings also cover an industrial area of interest. Among the most important fields of application we can highlight the following ones: packaging glass, glass sheets for furniture and sanitary appliances, glass in architecture and the building industry and glazing in the automotive sector. Here, two examples of hybrid coatings on glass will be presented, but colour coatings can also be applied on mineral or metal surfaces.

The first example is illustrated in Fig. 10(a) and represents a dishwasher-safe ORMOCER® colour coating on glass (DEKOSIL®). The main advantages in terms of the processing of these coatings are the easy reproducibility of the colours and the finishing by conventional wet painting procedures (low curing temperatures <200 °C). Furthermore, from an aesthetic point of view, some requirements such as an unlimited colour palette, additional decorative effects like colour gradients or partial coloration are accomplished as well.

The second example concerns titania siloxane based hybrid organic–inorganic materials that have been developed by several glass packaging industries in Japan[132] and in Europe. These coatings (illustration in Fig. 10(b))[132] can not only give access to a wide variety of colours, enhancing the consumer appeal, but they also allow an improvement of the mechanical properties of glass bottles. Moreover, these dye coloured bottles are easy to recycle as uncoloured glass (these materials do not need colour classification recycling) because, in contrast to conventional glass bottles, their coloration does not arise from transition metals that are very difficult to removed upon re-melting.

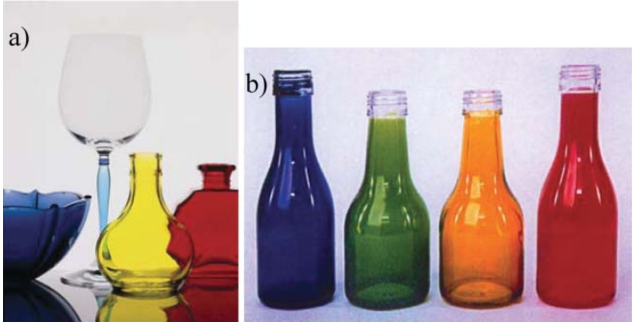


Fig. 10 Two examples of hybrid coatings with decorative interest: (a) glass ware demonstrating the high quality optical appearance of crystal glass and other types of glasses coated with dye coloured hybrid coatings (courtesy of Fraunhofer ISC);[115] (b) easy to recycle coloured glass bottles coated by hybrid organic–inorganic materials.[132]

III.3.c. Hybrid materials as barrier systems[133–140]. The interest in hybrid materials as barrier systems has been increased in the last decades as a result of the requirements to develop much more sophisticated materials in fields such as solar cells, optics, electronics, food packaging, *etc*.

New barrier coating materials based on ORMOCER® have been developed by Fraunhofer ISC which together with a vapour-deposited SiO_x layer guarantee sufficient protection to ensure a long durability of encapsulated solar cells (see Fig. 11(a)). This new inorganic–organic hybrid coating represents a whole encapsulation system since apart from the physical encapsulation it acts as an adhesive/sealing layer barrier against water vapour and gases, as well as an outside layer for weatherability. All these functions are combined in one composite ("one component encapsulant") and in this way the overall cost reduction for encapsulation reaches about 50 per cent.

The flexible nature of this hybrid material results in an optimized encapsulation process and especially in good protection of the edge area, the most difficult part for protection. Furthermore, this new material can be used from the roll, thus providing easy handling and automation in the

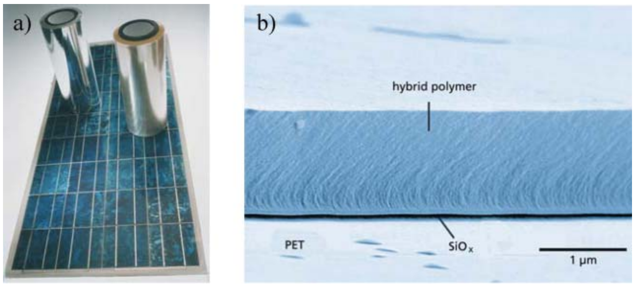


Fig. 11 Hybrid coatings as barrier systems. (a) Aspect of the hybrid coated solar modules with very high barrier properties. (b) Scanning transmission micrograph of a thin hybrid polymer coating on SiO_x deposited on a flexible PET film. (Courtesy of Fraunhofer ISC).

production of flexible modules (Fig. 11(b)). Thin barrier layers like SiO_x combined with ORMOCER® based barrier coatings save material and energy consumption in the production of the new encapsulating material. Therefore, a material and energy saving encapsulation technology is achieved. This result should encourage the application of thin film solar cells in the building industry as well as the number of users of solar cells.

Especially flexible thin film solar cells cover broader fields of application because they can be adapted to non-planar surfaces. This means that photovoltaic (PV) devices could be a standard integrated part of construction components, in *e.g.* roofing materials, façades, and balustrades. Thus, a larger number of potential users could benefit from solar technology. Upcoming and future products require flexible films that have high barrier or even ultra-high barrier properties. The encapsulation film for solar modules is one important example which illustrates that there is still a great need for the development of improved polymer barrier systems. The basis of most of the barrier coatings are polycondensates of some percentage of Al alkoxides with phenyl- and epoxy-functionalised alkoxysilanes.

Further developments on patternable barriers/passivation with good dielectric properties for application in roll-to-roll processing of polymer-electronic devices and systems are on the way for up-scaled technology and production at Fraunhofer ISC.[141]

Sol–gel chemistry has been extensively applied to produce thin oxide coatings with appropriate protective behavior onto metal substrates.[142] Nevertheless, protection of metallic silver reflectors, for example, should resist not only gaseous oxidation but also mechanical and chemical attacks during handling, cleaning or weathering of the metal parts. Laser labs have developed a silica-based hybrid material to protect silver-coated light reflectors installed in laser pumping cavities as shown in Fig. 12.[143] These metallic reflectors require a protective overlayer in order to preserve the high-reflectivity front surfaces for long periods of operation under intense broadband flashlamp light and typical airborne contaminants. The organically modified silica coating has been optimized in terms of thickness and composition to enhance metal resistance to oxidation and tarnishing under UV-irradiation and ozone-attack. To fulfil these requirements, the hybrid sol–gel material not only must act as an oxidation dense barrier but also needs to be chemical-resistant, time-stable and to remain transparent. On the other hand, industrial protective coating deposition onto large-sized and multi-shaped metallic parts is allowed by using the dip-coating technique.

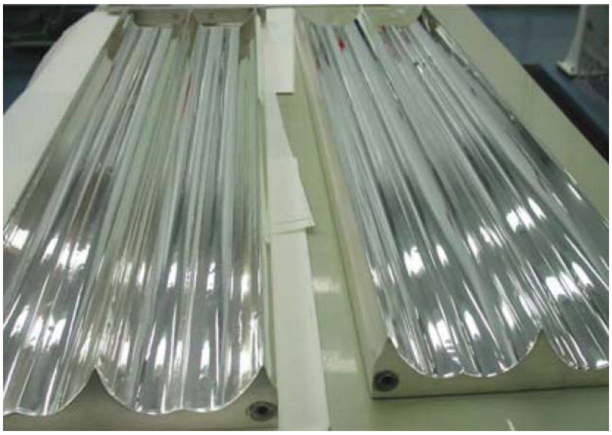


Fig. 12 Silver metallic reflectors used in laser-cavities dip-coated with a hybrid silica-based protective layer (courtesy of CEA).

The protection efficiency is mainly related to the density of the hybrid coating, and can be managed varying the sol–gel chemistry conditions (hydrolysis rate) and oxide content. Furthermore, hybrid material compared to pure inorganic allows one to enhance the chemical resistance through incorporation of hydrophobic surface functions, such as methyl groups, which also reduce coating stress allowing a thicker film deposition onto eventually deformable substrates. This hybrid layer preserves the high reflectance of silver over a broad spectral range and enables silver reflectors to withstand a very corrosive medium with no appreciable degradation.

III.3.d. Hybrid materials for dental applications[144–149].

Inorganic–organic hybrid materials can be used as filling composites in dental applications. As schematized in Fig. 13(a), these composites feature tooth-like properties (appropriate hardness, elasticity and thermal expansion behaviour) and are easy to use by the dentist as they easily penetrate into the cavity and harden quickly under the effect of blue light. Moreover, these materials feature minimum shrinkage, are non-toxic and sufficiently non-transparent to X-rays. However, the composition of the hybrid material and the chemistry behind it depends strongly on its later application: as filler/particles, as matrix materials, as composites, as glass ionomer cements or as bonding.

Traditional plastic filling composites had long-term adhesion problems and a high degree of polymerisation shrinkage resulting in marginal fissures. The dual character of the ORMOCER®s as inorganic–organic copolymers is the key for improving the properties of filling composites. The organic, reactive monomers are bound in the sol–gel process by the formation of an inorganic network. Thus, in the subsequent curing process, polymerisation takes place with less shrinkage. Furthermore, abrasion resistance, in particular, is significantly enhanced by the existing inorganic Si–O–Si network.

For example, in dental fillers organic functionalities including ring-opening reactions, such as functionalized spyrosilanes, are commonly included in the hybrid network. Other systems are based on multiacrylate silanes, offering a high organic density. In addition, mechanical properties of the composite can be tuned through variation of the spacer between the silicon atom and the reactive functionality. All these possibilities are already taken into account, and most of these hybrids include various fillers in their composition.

As examples of available commercial filling composites based on dental ORMOCER®s from Fraunhofer ISC one can appoint "Definite®" and "Admira®" (Fig. 13(b)). In the case of the Admira® product, a specifically designed dentine-enamel bonding, an adhesive ORMOCER® developed in cooperation with VOCO GmbH, is used to make this product especially advantageous.

In glass ionomer cement based dental composites blue light polymerisable carboxyl functionalised ORMOCER®s have

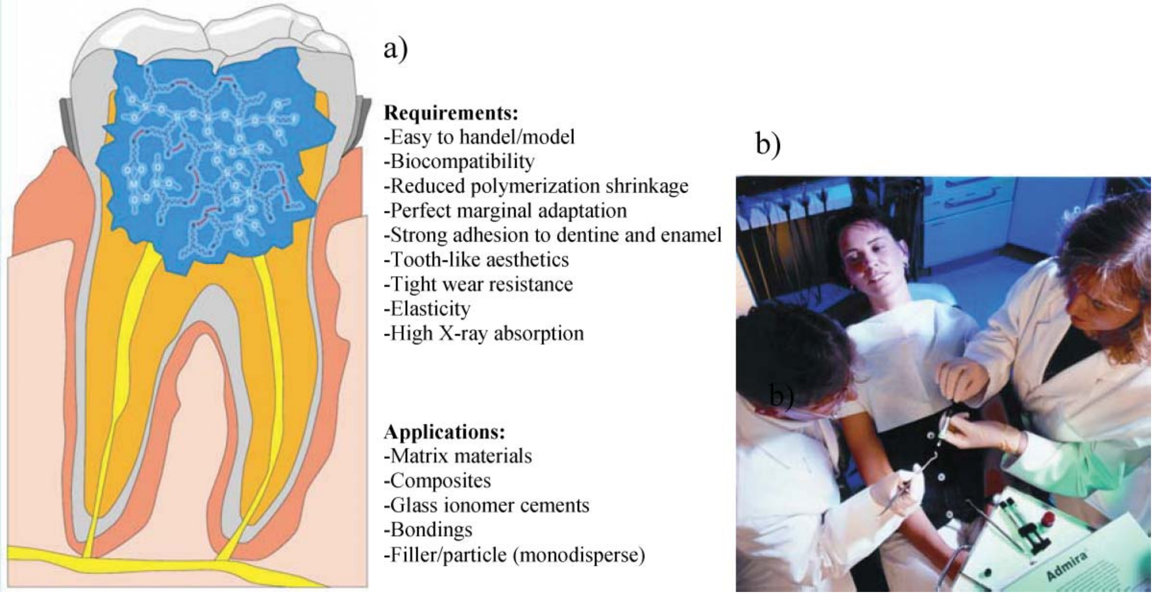


Fig. 13 (a) Requirements and possibilities of dental applications of ORMOCER$^{®}$s. (b) Application of an ORMOCER$^{®}$ as dental filling material.

been developed. In this case, the cement forming reaction compensates the shrinkage resulting from organic cross-linking reaction of *e.g.* methacryl functionality.

III.3.e. Hybrid materials for microelectronics$^{150–167}$. Organically modified resins retain important roles in electrical component coatings such as resistors and molding compounds, as well as spin-on dielectrics in microelectronic interlayer and multilayer dielectric and planarization applications.

Simply methyl or hydride substitution of alkoxysilanes allowed the development of commercial products such as: Glass-Rock$^{®}$ by Owens–Illinois, for sealing cathode-ray tubes; Techneglas$^{®}$ by NEC, for dielectric applications, Accu-Spin$^{®}$ by Honeywell, for spin-on glass applications, *etc*. However, although numerous commercial hybrid-based products in electronics merit mention, only several representative examples will be detailed.

To demonstrate the feasibility of ORMOCER$^{®}$s for use as an MCM L/D material, a substrate for a Pentium™ multi-chip module (MCM) with a BGA interface was realised (see Fig. 14(a)). The substrate of that demonstrator consists of a metal interconnection separated by ORMOCER$^{®}$ dielectrics on top of a FR-4 laminate including power and ground planes. Two sputtered aluminium layers were used for the signal interconnection. The signal layers were separated from each other and from the power plane by 6 μm thick spin-coated ORMOCER$^{®}$ layers in which via-holes were defined by direct photo-patterning. The FR-4 laminate was provided with micro-vias and through hole vias connecting to a 1.27 mm pitch, ball grid array underneath.

In Fig. 14(a), from right to left, the different steps of sequentially built-up (SBU) processing are given: Cu-metallised FR-4-substrate (ground plane), first ORMOCER$^{®}$ layer with power plane, second ORMOCER$^{®}$ layer with first signal plane, third ORMOCER$^{®}$ layer with second signal plane, and finally a Pentium™ chip set was also mounted on the substrate. This example shows the possibilities offered by low temperature curing of hybrid materials to achieve compact low cost devices by integration of the MCM substrate with the package.

As these hybrids show beside good dielectric and processing properties also high optical transmission, opto-electrical (o/e) and opto-electronic applications were done. The concept enabled by ORMOCER$^{®}$ technology aims at very low cost and comprises high density electrical interconnects and optical waveguides integrated in three layers of ORMOCER$^{®}$s. In Fig. 14(b) an optoelectronic-MCM-L/D demonstrator is depicted (an electro-optical board, laminate with a hybrid in SBU-technology on top as well as a 5-channel optical transmitter and a 5-channel optical receiver). The thin film layers have been put on top of an FR-4 laminate with micro-vias. The laminate is furnished with a ball grid array (BGA) underneath, eliminating the need of any extra package.

The advantage of tuning the hybrid's flexibility and adhesion properties allows their use on flexible substrates, even as optical waveguides. Fig. 15 shows ORMOCER$^{®}$ waveguides in which the hybrid coating is deposited on a flexible foil.

The chemistry of these hybrid polymers is based on the 1 : 1 polycondensation (alkoxolation) of diphenyl silanediol and

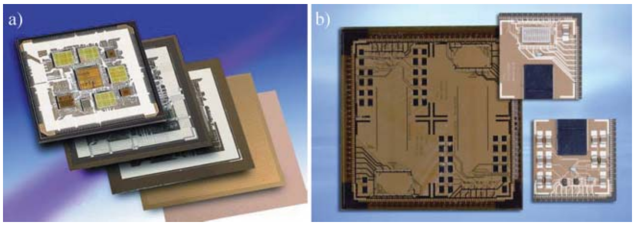


Fig. 14 (a) Smallest-sized Pentium$^{®}$ MCM-L/D manufactured in ORMOCER$^{®}$ multi-layer technology (ERICSSON/ACREO). (b) Electro-optical (o/e) MCM manufactured in ORMOCER$^{®}$ multi-layer technology (ERICSSON/ACREO/Motorola).

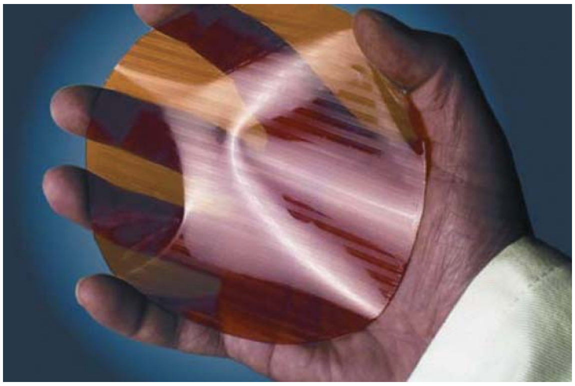


Fig. 15 ORMOCER® waveguides on a flexible foil.

silicon trialkoxides with methacryl and/or epoxy respectively cyclohexylepoxy functionalities. The ''water-free'' alkoxolation reaction causes condensates nearly free of residual SiOH, essential for low optical loss in the near infrared around 1550 nm. The high aryl content is chosen to get also a low-loss window in the NIR around 1310 nm. This easy chemistry therefore offers a perfect fit for implementation as an optical waveguide material in systems like transmitters and receivers in medium and long distance telecommunication, thermo-optical switches and couplers *etc.*, as the laser-sources as well as the glass-fibres work in these low-loss windows. Having a low permittivity ε around 3.5 that composition could also be in parallel used as dielectrics. Because of the methacryl group such systems are photo-definable *i.e.* they can be used in photolithography, projection lithography as well as all kinds of UV-laser technology.

Dielectric ORMOCER®-hybrid polymers offer perfect media for high resolution photolithography because: (i) the precursor oligomers of the siloxane part have a small size around 1–5 nm, and (ii) the chemical cross-linking during mask-aligning (UV-polymerisation based patterning) is strongly sterically hindered by the oligomers which cause a fast break-down of radical polymerisation avoiding parasitic reactions into the mask-shaded areas. In general, their chemistry is based on the polycondensation of phenyl-functionalized silanols with tetraalkoxysilane as well as some percentage of zirconium alkoxides. As reactive cross-linking species such as silanes with methacryl groups (UV-polymerisation) and epoxy groups (thermal postcuring) can be used.

Recent publications give information about the use of ORMOCER® hybrids for 2-photon-polymerisation within femto-laser technology. It allows by careful choice of photo-initiators very high resolution for *e.g.* build-up of photonic crystals. Here, an additional benefit of hybrids: the mechanical stability allows the build-up of very fine structures <100 nm.

III.3.f. Hybrid materials for micro-optics[168–174]. Wafer-scale UV-embossing can be applied to substrates other than glass, for example Si and semiconductor III–V based wafers with prefabricated devices. In these cases, it is often advantageous to use the same hybrid materials in a combined lithographic and embossing mode to produce free-standing micro-optical elements, for example the lenslet on VCSEL elements for fiber coupling (CSEM in collaboration with Avalon Photonics Ltd., CH-Zurich). Fig. 16 shows SEM images of processed micro-optical components on VCSEL wafers: (a) diffractive lenses, (b) an array of refractive lenses.

All the Pyramid Optics' collimator arrays shown in Fig. 17 are constructed with a silicon V-groove fiber array mounted with a microlens array. The microlens arrays are replicated in a ORMOCER® thin film on a BK7 glass substrate.

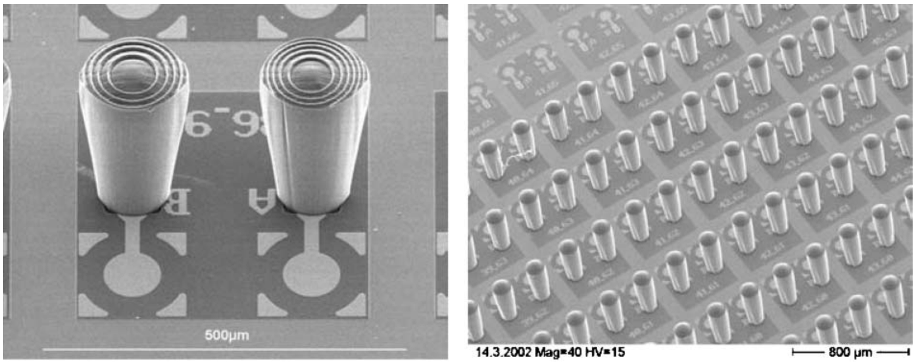


Fig. 16 Scanning electron micrographs of a lens array on VCSEL (courtesy of CSEM/Avalon).

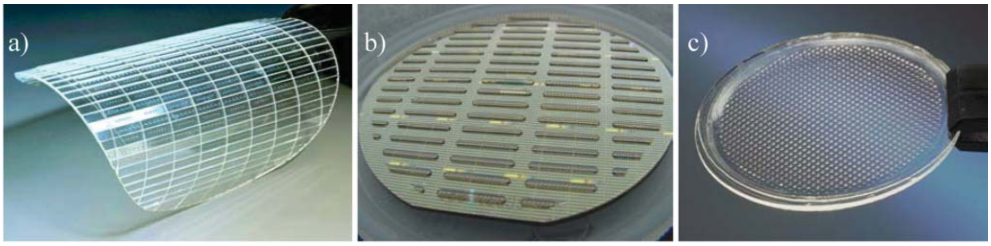


Fig. 17 (a) Sawed lens wafer: ORMOCER® based micro-lenses on glass. (b) ORMOCER® based collimation micro-lens arrays on InP VCSELs. (c) Large microlenses on glass substrate (BK7) (courtesy of Fraunhofer IOF).

The new collimator arrays are offered for several wavelength regions: 630–690 nm; 780–850 nm and 1250–1650 nm. Other wavelengths are possible on request.

Several of the above used hybrids for optical applications are now licensed by Fraunhofer-ISC to the company Micro Resist Technology GmbH and they are producing them in large scale and marketing them worldwide under the names: "Ormocore", "Ormoclad" and "Ormocomp". As a result, besides the given industries, lots of companies from Japan and South Korea as well as from Europe (Germany, Switzerland, Sweden, and Finland) have integrated these materials mostly in micro-optical products.

Nanohybrids are also used for interference optical coatings. Dielectric mirrors or reflectors can be prepared using interference quarterwave stacks of colloidal-based low-refractive index material and a hybrid dense material as the high refractive index layer. In the literature, a possible high index layer used for laser optical thin films[139] is a nanohybrid material prepared from mixing a nanosized-zirconia suspension with a transparent polymer alcoholic solution.

Using a hybrid system with a polymeric binder in the high index oxide sol helps to decrease the total layer number required for the same reflection value. The selected polymer must be soluble in the suspending medium, preventing the sol from flocculation, and also needs to be transparent at the wavelength of interest. That is the reason why polyvinylpyrrolidone (PVP) was chosen as possessing the best combination of properties for binder use. Considering the structure of the monomer unit, it is seen to have an amphiphilic character. Indeed, PVP contains a highly polar amide group conferring hydrophilic and polar-attracting properties, and also apolar methylene (CH_2) and methine (CH) groups in the backbone and the ring conferring hydrophobic properties. When added to a colloidal suspension, the amphiphilic character of PVP helps to maintain colloidal stability and to reduce flocculation through a steric stabilization mechanism.[175]

As the purpose was to get the maximum refractive index value, the oxide/polymer ratio of the hybrid system needed to be optimized. It was demonstrated that the index value was directly dependent on the PVP/oxide ratio and the optimum ratio was determined in a separate experiment in which the hybrid refractive index variation was plotted regarding the PVP/oxide ratio (see Fig. 18).[176]

The PVP polymer is supposed to "smother" the oxide nanoparticles leading to a dense hybrid structure with hydrogen-bonding between the amide carbonyl groups of PVP and surface hydroxyl groups of oxide particles (Fig. 19). A similar dense hybrid structure was described by Toki *et al.*[177] for silica nanosized particles.

Because PVP was soluble in alcoholic solvents, multilayer deposition required a UV-curing step to avoid redissolution of the previous deposited polymeric layer. PVP is a photosensitive polymer that could be UV-cured using short wavelength irradiation. In the UV-curing of PVP, FT-IR measurements show that the increase of the hydroxyl-band is correlated to the decrease of the ketone and amide bands. This UV-induced hydroxylation of PVP explains the modification of its solubility because, as for polyvinyl alcohol (PVA),[178] crystallinity of hydroxylated-PVP (OH-PVP) has changed.

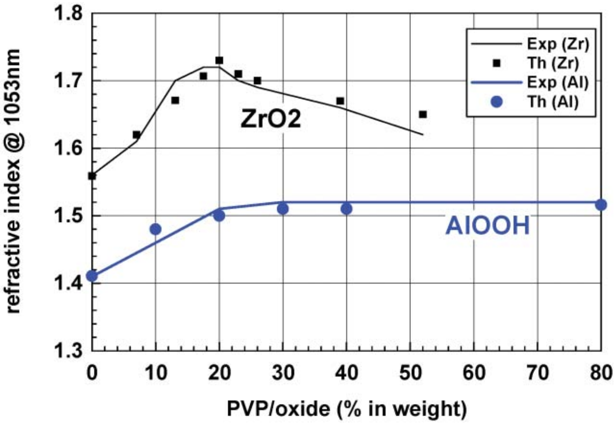


Fig. 18 Coating refractive index variation depending on the (polymeric filler/oxide) film ratio, for hybrid zirconia and alumina sols (solid lines correspond to Drude's model predictions).

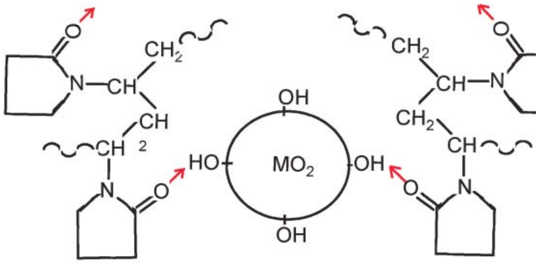


Fig. 19 Schematic view of PVP and oxide colloid bonding.

Using such nano-hybrid materials, 99.5% reflection coatings have been prepared on a 42 × 46 × 9 cm deformable mirror (BK-7 substrate) for near infrared use (1053 nm wavelength) exhibiting high optical uniformity and low optical losses (as low as 0.35%) (Fig. 20).[179]

III.3.g. Hybrid materials for batteries:[180–186] gels as ionic conductors. Electrolytes for use in lithium batteries have to be free of Si–OH-functionalities, as otherwise hydrogen forms, which must be strictly avoided. Si–OH-functionalities can be prevented either by choosing appropriate solvents and catalysts during synthesis or by the reaction of remaining Si–OH with tri-substituted alkoxysilanes.[184,185]

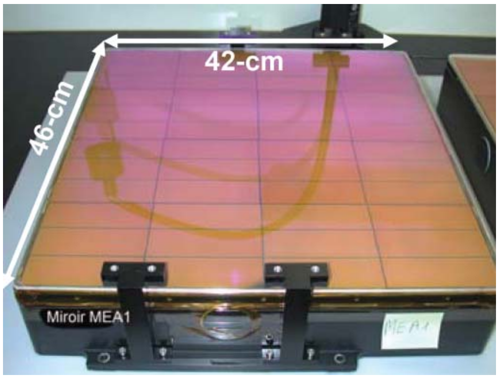


Fig. 20 Deformable laser-cavity mirror coated with a sol–gel nanohybrid multilayer optical stack.

By specific choice of functionalized alkoxysilanes and addition of plasticizers conductivities of up to 10^{-3} S cm^{-1} can be achieved[186] while a good mechanical stability is also maintained. These materials are electrochemically stable up to 4.2 V. Prototype battery production based on an up-scaled ORMOCER® electrolyte separator from Fraunhofer ISC has started at Varta Company.

Recent developments at the Fraunhofer ISC aim at systems which can be applied without adding liquid plasticizers. Such electrolytes will have enhanced dimensional stability. So, very thin electrode foils without further encapsulation measures can be used. Such electrolytes have reached conductivities of about 5×10^{-5} S cm^{-1} at room temperature until now. These values are below those for systems containing liquid plasticizers but they are sufficient for only 20 μm thick layers which are achieved in the battery concept. This conductivity in addition to an electrochemical stability of 4.2 V shows the very high potential of this new electrolyte for thin film lithium–polymer batteries (see Fig. 21).

In parallel and in cooperation at LEPMI-INPG, organic–inorganic gels have also been synthesized by interchanging some alkoxy groups of $Si(OR)_4$ precursors with polyethyleneglycol (PEG) chains. The PEG was used to solvate small cations such as lithium, leading to a good ionic conductivity.[181] However the slow hydrolysis of the Si–O–PEG bonds leads to a degradation of such materials. This stability problem can be avoided by using AMINOSILS.[181] These compounds were recently synthesized *via* the hydrolysis and condensation of $Si(OR)_3R'$ precursors ($R' = –(CH_2)_n–NH_2$). The non-hydrolyzable alkylamino group can solvate, *via* the amino group, anions such as $CF_3SO_3^-$ rendering free for conduction the associated counter ions (protons). The resulting gels exhibit a rather good protonic conductivity at room temperature ($\sigma = 1.4 \times 10^{-5}$ S cm^{-1} for $Si(OR)_3(CH_2)_3NH_2,(CF_3SO_3H)_{0.1}$ based systems).[181,187]

Among electrochemical devices, electrochromic displays using transition metal oxides (WO_3, TiO_2, MnO_2, IrO_2) as active electrodes can be built by using protonic conductor gels as electrolytes. However, in such acidic conditions and upon electrochromic solicitations the oxide layers are corroded, because the stability of many oxides lies in the 4 to 12 pH range. To overcome this problem, new proton vacancy conducting transparent polymers which work in a higher pH range were developed.[183] However when the different components (POE, sulfamide, guanidinium cation) are mixed without covalent bonding between the different phases, the resulting polymer electrolyte is in a metastable amorphous state. Slow crystallization responsible for a drastic decrease in conductivity occurs in a few month of storage. In order to overcome both acidity and crystallinity problems, new proton vacancy conductors based on anion-grafted ormosils have been synthesized *via* a sol–gel process. These ionic conductors are based on a three component system: a solvating polymer (α,ω-di-(3-ureapropyltriethoxysilane)poly(oxyethylene-*co*-oxypropylene)), a proton source (3-methanesulfonamidopropyltrimethoxysilane) and a deprotonating agent or proton vacancy inducer (imidazolium cations introduced through 3-(2-imidazolin-1-yl)propyltriethoxysilane, where imidazoline is used as a strong base).[183] These materials are obtained by the copolymerization of sulfonamide-containing groups, partially deprotonated, and POE as an internal plasticizer. All organics groups are anchored to trialkoxy silanes which, through hydrolysis and condensation reaction, lead to a silica based backbone. In the presence of a deprotonating agent, conductivity is greatly enhanced, being now solely due to the motion of proton vacancies. The conductivity is 10^{-5} S cm^{-1} at 80 °C.

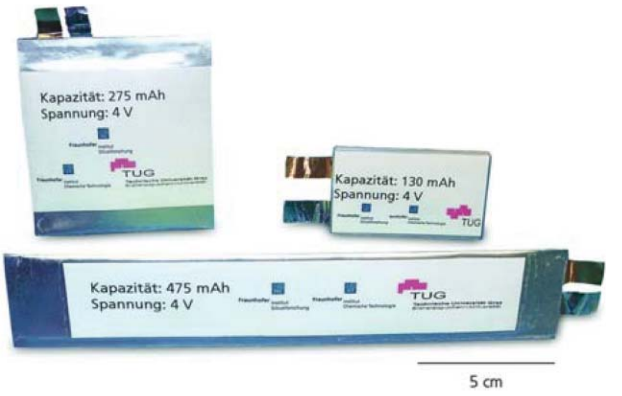


Fig. 21 Samples of flexible thin film batteries.

III.3.h. Use of sol–gel hybrids for photovoltaic cell application. Up to now, the main photovoltaic (PV) devices are based on solid-state junctions, usually made of silicon and are profiting from the development of the semiconductor industry. In this situation, a challenging new generation of solar cell is emerging, based on the use of interpenetrating network of nanocrystalline oxide and conducting electrolyte.[188]

The so-called dye-sensitized solar cell (DSC) constitutes a promising technical and economical alternative to p–n junction photovoltaic devices. Unlike the conventional silicon systems in which the semiconducting material supports both the light absorption and charge carrier transportation functions, in the DSC the two tasks are split. Light is absorbed by a sensitizer, which is anchored to the surface of a wide band gap oxide semiconductor. Charge separation takes place at the interface *via* photon-induced electron injection from the dye into the conduction band of the solid. Charge carriers are then transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline structure allows the collection of a large fraction of sunlight. The intimate penetrating network of mesoscopic oxide and conducting electrolyte competes today with the conversion efficiency of conventional solid-state devices. They reach in the case of TiO_2 as semiconductor, ruthenium-based complex as dye and redox couple-containing liquid as electrolyte, an overall solar (standard AM 1.5) to current conversion efficiency of 10.4%.[189] Although the efficiency of light conversion is spectacular in these systems, one limitation is the liquid electrolyte-based DSC approach using low viscosity, highly volatile solvents (*e.g.* acetonitrile) which hinder commercialization spreading. A number of solutions have been proposed to solve this problem. One includes replacement of the liquid junction with a conducting ion gel electrolyte,[190] with inorganic materials such as p-type CuI, CuSCN or with organic hole conductors such as triphenyldiamine (TPD) or polypyrrole[191–195] or substituted polythiophenes.[196,197] This third generation of PV cell is very promising and overall efficiencies from 3.2 up to 3.8% have been obtained.[198,199] Such all-solid-state organic–inorganic hybrid dye-sensitized solar cells intend to eliminate practical problems of liquid electrolyte use like degradation with time, cell sealing, handling, technological aspects of module production. Nevertheless, one needs to completely understand and control the interface between the organic and the inorganic portions of the PV cell in order to facilitate reactions occurring at the interface. Among the critical parameters, a major one is the spreading of the interaction between each working layer of the PV cell stack. Especially, the inorganic layer plays an important role in hybrid DSC, accepting an electron from the excited state of the dye and preventing recombination of the newly formed electron–hole pair. In order to increase the efficiency of the sunlight harvesting area, a fractal TiO_2 semiconductor oxide layer prepared by the sol–gel chemical method has been replaced with a nanostructured thin film first deposited from colloidal suspensions. This route evidently provides a much more reproducible and controlled interacting porous high surface area. The optimized material used in hybrid solar cells is prepared using the hydrothermal synthesis of Brooks,[200] which enables the preparation of size-controlled nanoparticles impacting onto the nanostructure and porosity of the semiconductor layer. In this approach, there is no need to dope the oxide film since the injection of one single electron from the surface adsorbed sensitizer into a TiO_2 nanoparticle is enough to make it conductive. Moreover, such mesoporous thin films having high surface roughness do not promote charge carrier loss due to recombination. Among new trends, new developments are directed towards synthesis of structured new materials having desirable morphology like mesoporous channels or nanorods aligned perpendicular to the transparent conducting oxide glass.[201,202]

A new promising work reports the development of mesostructured materials using the evaporation-induced self-assembly of surfactant templates in the reaction medium.[203,204] Porous ordered structures of mesostructured semiconductor oxides compared to former random particle networks are supposed to simultaneously optimize the P–N surface area, the pore filling with the hole conductor polymer, charge carrier transportation and percolation. The use of an inorganic mesophase structure in the PV cell opens a large field of investigation in relation with the numerous accessible organized structure of the porosity (like the 3-D cubic *Im*3*m* phase) which can be optimized for enhanced energy conversion efficiency and therefore solar cell performance[205] (Fig. 22).

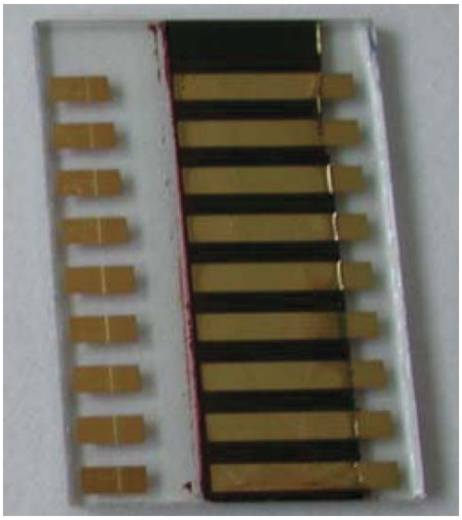


Fig. 22 First all solid-state nanohybrid dye-sensitized prototype solar cell containing mesostructured titanium oxide as the semiconductor. An energy conversion efficiency of 1.3% has been measured (courtesy of CEA).

III.3.i. Use of sol–gel hybrids for proton-exchange membrane fuel cell (PEMFC) applications. In the fuel cell core, the main important part for cell efficiency and durability is the proton exchange membrane.[206] Its role is to allow proton transport from the anode to the cathode, to be an electron non-conductive material and to act as a gas separating barrier (H_2, O_2). Typical membranes are made of organic polymers containing acidic functions such as carboxylic, sulfonic or phosphonic groups which dissociate when solvated with water, allowing H_3O^+ hydrated proton transport. Therefore, the membrane performance is related to the ionic group amount and to the hydration rate. Moreover, the membrane needs to be chemically (highly acidic medium) and thermally (from 80 to 140 °C) stable.

In this sense, proton conducting polymers such as poly(benzylsulfonic acid) siloxane (PBSS) with very high proton conductivity has been prepared by a sol–gel process.[182] The synthesis occurs in 2 steps: (i) triethoxybenzylsilane is first hydrolyzed and self condensed into a polybenzylsiloxane polymer (PBS), reaching an average molecular weight M_w = 20000, in the presence of trifluoromethanesulfonic acid as a catalyst, and then (ii) the sulfonation of PBS into PBSS is carried out in anhydrous dichloromethane. The PBSS obtained is thermally stable up to 300 °C. Moreover, the high conductivity (σ ranges from 2×10^{-3} to 10^{-2} S cm^{-1}) of PBSS, as well as its tensile strength, allow its use in several electrochemical devices at room temperature. Alternatively in ORMOCER®s, for use as proton conductors sulfonic acid was attached *via* the Si-propyl-chain to the hybrid matrix.[207–211] Depending on the concentration of the sulfonyl groups, and water or imidazole as proton-carrier, conductivities of 5×10^{-5} at RT for water-free sulfonyl-sulfonamide donor–acceptor systems to water containing systems with similar conductivity like Nafion™ could be achieved. Newest results by use of imidazole replacing the water, allow working at elevated temperatures of 140 °C with conductivities above 10^{-2} S cm^{-1}. According to the heavy redox-potential in fuel-cells and the needed thermo-mechanical properties those systems are still in the testing phase.

Besides the requirements mentioned above, the material needs to be also a low-cost product to allow the spreading of such low-temperature fuel cell technology. Today, only perfluorinated polymers containing sulfonic groups are competitive for use in PEMFC or DMFC (direct methanol fuel cell) systems. Commercial membranes can be Nafion®

(Dupont de Nemours[212]), Dow® (Dow Chemical[213]), Flemion® (Asahi Chemical) or Aciplex-S® (Asahi Glass[214]). Nevertheless, all these materials are porous to methanol, expensive to mass-produce and are overall limited to low-temperature operation. However, the use of a PEMFC membrane at higher temperature (above 80 °C) is needed principally to increase cell yield required for high-consumption applications like transportation. Alternative materials to Nafion® are consequently the aim of numerous research topics around the world: searching for highly proton conductive membranes, high-temperature water-keeping property (beyond 100 °C) and made of low-cost thermoset polymers. Among the potential materials, aromatic-based polymers such as polysulfones,[215] poly(benzimidazoles),[216] poly(imides) or poly(aryletherketones), so-called PEEK,[217] are possible candidates but they need to be functionalized with sulfonic groups to become conductive.

Another route to substitute the Nafion® is to prepare either a nanocomposite material[218] or an organic–inorganic hybrid polymer.

The nanocomposite membrane is made of a polymeric matrix in which an inorganic phase is incorporated. The so-added phase is hydrophilic and therefore helps to retain moisture inside the membrane when d at high temperature. Conductivity is maintained and can be also enhanced when using an inorganic phase grafted with conductive groups (acidic or sulfonic functional groups). The inorganic phase is mostly oxide particles (SiO_2, Al_2O_3, TiO_2, ZrO_2) which can be mixed with Pt nano-crystals to help self-moisturizing of the membrane,[219] or based on clays[220] or zeolites.[221] The last two examples are interesting materials since both of them exhibit porosity (flexible or rigid respectively), enabling the storage of water above 100 °C. More often used clays are smectite-based: montmorillonite (natural) or laponite (synthetic). Such clays added to a sulfonated-PEEK polymer increase moisturizing, mechanical, thermal and chemical stability and proton conductivity of the composite membrane high enough to compete with Nafion® 115 performance.[222] Besides the water retention, the nanocomposite load should also prevent loss of total conductive group amount due to the incorporation of clay (decrease of ion-exchange capacity or IEC). This can be avoided with the functionalization of the mineral phase before mixing with the polymer. For example, the grafting of sulfonic groups to laponite-type clays *via para*-styrene sulfonic acid reaction enables the IEC of the composite membrane to be increased.[223] The contribution of a modified mineral phase homogeneously dispersed in the polymeric matrix is today demonstrated (see Fig. 23). The modification of the clay to make it conductive allows the consideratin of Nafion® replacement with non-conductive but high-performance polymers such as PVDF or PVDF-HFP.

In the manner of the clays, the organic–inorganic hybrid approach is also very promising for fuel cell membrane ultimate development. The main advantage of the hybrid membrane consists of the *in-situ* growth of the inorganic phase inside the polymeric matrix which gives rise to a highly-dispersed and highly-organized material. Zoppi *et al.*[224] and Mauritz[225] were the firsts to describe the preparation of "hybrid-Nafion®" membranes with *in-situ* growth of colloidal silica. The main contribution of silica is to maintain the hydration rate regarding temperature increase to the detriment of the IEC. Wang *et al.*[226] have therefore prepared hybrid membranes with higher conductivity compared to Nafion® using a sulfonated nanoparticle silica phase. Another innovative idea is to use a mesoporous silica (Hamoudi and Kaliaguine[227]) or a mesostructured phase (CEA[228,229]) which can be modified to make it conductive. The very high and structured porosity of these new hybrid membranes enhance the water storage, the intimate mixture of polymeric chains with inorganic phase and mostly the exchange capacity (IEC) through a much larger surface area available for functionalization. Authors have recently demonstrated that the embedded-growth of a high exchange surface area silica ordered network in an organic polymeric matrix enables the preparation of a very complete hybrid membrane.[230] Indeed, this novel approach gathers together complementary essential properties: first, water uptake control due to the open mesoporosity; second, the enhancement of proton conductivity values when the membrane operates at high temperature and low relative humidity rate thanks to the adequate grafting of sulfonic moieties in the silica phase, allowing moreover the use of a non-conductive polymer such as PVDF for example; third, the mechanical property of the membrane, in which the formation of a finely-dispersed mesostructured inorganic network leads to a flexible and non-swelling homogeneous material, that withstand repeated thickness variations during the lifetime of the cell.

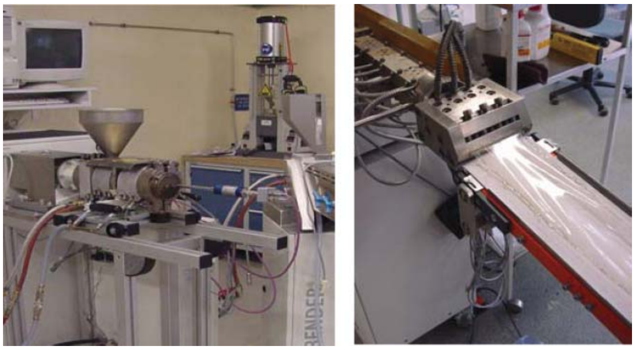


Fig. 23 Extruded nanocomposite PEMFC membranes are prepared using clays as inorganic moisturizing phase (courtesy of CEA).

The end of the Nafion® monopoly, a perfluorinated polymer originally developed as an improved material for electrolysis membranes in chlor-alkali production, seems to be more and more attainable.

III.3.j. Other applications of sol–gel hybrids. Another application of sol–gel derived hybrid materials not mentioned until now is as adhesives. In this field, the best examples of inorganic–organic hybrids are the organically derived siloxane resins. They are made of SiO_2 units cross-linked with trimethylsiloxy or hydroxyl groups, and exhibit molecular weights of 2000 to 10000. Their larger application concerns the pressure-sensitive adhesives (PSAs).[231,232] Furthermore, these resins are also used in cosmetics, water-repellents and additives for paper release coatings.[233]

The functionalisation of polypropylene oxide with organically modified silanes results in a liquid polymer that cures in the presence of moisture to form conformable low-cost sealants and caulks.[234] This technology has been commercialized by Kaneka.

Polyethylene exhibits a desirable balance of electrical, mechanical and processing properties that has led to its acceptance as a wire and cable insulation material. However, the low continuous operating temperature of this polymer (70 °C) must be increased in order to enlarge its applications as insulating material. Traditionally, this temperature was increased to more than 90 °C by peroxide and radiation cross-linking, but this treatment has been supplanted by methods involving cross-linking of alkoxysilanes. At present, the technology of hybrid materials is widely accepted in wire and cable insulation (telephone and medium-voltage power cables) and in heat-shrinkable tubing and compression-resistant foam. Thus, companies that practice the graft technology are Equistar (formely Quantum Chemicals), BICC, Alcan and Okonite.

These kind of derived siloxane–polyethylene hybrid polymers were also used to fabricate thermoplastic equipment in the automotive industry, and indeed, Mitsubishi patented this technology,[235] but other companies such as Neste (VISICO®), Union Carbide (SI-LINK®) and AT Polymers (Aqua-Link®) have also commercialized these hybrid copolymers.

Special mention must be made of aerogels, since they are unique among solid materials. They exhibit extremely low density, large open pores and a high inner surface area. These interesting physical properties related to the specific drying procedure together with the versatility in chemical composition are very attractive for application in a large range of fields: windows and insulation, catalysis, sensors, optics, as catalyst carriers or even decoration.

Extensive literature can be found about the synthesis and applications of aerogels with pure inorganic, pure organic or inorganic–organic hybrid compositions.[236] Organic modification of inorganic oxide aerogels (SiO_2, TiO_2, ZrO_2, Al_2O_3, V_2O_5, *etc.*) allows the spectrum to be widened or their properties to be improved without influencing the intrinsic properties. Integration of organic components can be performed by embedding molecules during sol–gel processing, without chemical bonding (class I hybrids) but also by connecting organic and inorganic networks through organically derived alkoxysilanes (class II hybrids).

Among the interests of organic modification in aerogels, the enhancement of the stability under humid atmosphere (increase of hydrophobicity) and improvement of mechanical properties (augmentation of elasticity) are the most important topics. Schwertfeger *et al.* have studied the influence of organic components in tetraalkoxysilane (TEOS) and organically substituted trialkoxysilane mixtures, and permanently hydrophobic aerogels have been successfully prepared.[237] On the other hand, Kramer *et al.*[238] prepared aerogels with very good elastic properties by co-condensation of flexible polydimethylsiloxane (PDMS) with TEOS.

III.4. Hybrid nanocomposites constructed from functional NBBs

This section mainly refers to hybrid materials prepared through Path B (routes B1 and B2) described in Fig. 3.

III.4.a. Hybrid nanocomposites based on functional nanoclusters and nanoparticles. Sol–gel methods permit one to create nanometric and monodispersed inorganic "bricks", with great variety in their nature, structure and functionality (see Fig. 3, Path B). The use of NBBs as starting units to obtain hybrid organic–inorganic structures is an approach developed with various systems such as oligosilsesquioxanes and derivatives, organically functionalised heteropolyoxo-tungstates, organotin-oxo and transition metal-oxo clusters, organically pre- or post-functionalized nanoparticles (metal oxides, metals, chalcogenides, *etc.*), nanocore–shell or layered compounds able to intercalate organic components. Moreover, these NBBs can be capped with polymerizable ligands or connected through organic spacers (telechelic molecules or polymers, functional dendrimers). Their synthesis, structures and properties have been previously reviewed;[7, 239] therefore, in this review only the most promising NBB hybrid materials for real applications will be emphasized.

Inorganic components combined with COPs (Conducting Organic Polymers) can be used as electroactive, photoactive or catalytic agents providing the basis for their application in different types of devices (insertion electrodes in rechargeable lithium batteries or supercapacitors, electrochromic or photochromic components, display devices, LEDs, photovoltaics, or novel energy-conversion systems, as well as electrocatalysts, proton-pump electrodes, sensors, or chemiresistive detectors familiarly known as artificial "noses" or "tongues"). The first processable electrically conductive organic polymer was reported in 1992.[240] It was based on polyaniline doped with an anionic surfactant (dodecylbenzenesulfonic acid) and currently, this material is patented and commercialized by UNIAX Corporation, Neste Oy (Finland). Since then numerous commercial COP products have been developed in the field of sensors,[241] photovoltaic devices and solar cells,[242–246] LEDs,[247] actuators,[248] lithium batteries and capacitors,[249] *etc.*

Different types of polyoxometalates have been used to modify conducting polymers such as polyaniline, polyacetylene, polypyrrole, poly(*N*-methylpyrrole), and polythiophenes.[239a,250,251] These polyoxometalates act as large anions anchored in the polymer matrices and then, the resulting hybrid exhibits important consequences regarding the redox insertion mechanism. The permanence of the anions in the polymer, as a difference with mobile simple conventional anions (ClO_4^-), upon reduction forces the insertion of cations for the necessary charge balance, with the inverse process of cation expulsion taking place upon reoxidation, thus converting p-doped polymers into cation-inserting redox materials. This fact opens new possibilities for application in selective membranes, sensors and energy storage devices such as electrochemical supercapacitors or rechargeable lithium batteries. Two examples are: an electroactive hybrid formed by phosphomolybdate heteropolyanion and polypyrrole,[250] and a photoactive material based on a C_{60} derivative and MDMVO-PPV.[252] In the same research line, an extensively studied system is the family of hybrids based on V_2O_5 and conducting polymers such as polyaniline and derivates (PAni), polypyrrole (PPy) or polythiophenes (PT). Their main target application is as electrode for lithium batteries.[253,254] All these functional NNB hybrid materials are very promising but to our knowledge they have not reached commercial applications. They do however merit citation.

Surface modified nanoparticles by organic molecules or polymers offer additional advantages in processing because of their good dispersability in organic media and because they can also be directly molded.[26,255] Many applications concerning these hybrid nanocomposites (see Fig. 3, Path B1) are based on polymer encapsulated nanoparticles and therefore they require good coupling between the polymer matrix and the inorganic nanoparticles. Polymer modified nanoparticles offers prospects as carriers for catalysts or as toners for electro-photographic applications. Hybrid magnetic nanoparticles consisting of an inorganic core of metal, metal oxide or an alloy covered by organic polymers are of special interest. They can be used in magnetic recording media in tape or disc form, oil spill clean up and moldable magnetic powders. Furthermore, any organic or bio functionality can be attached to the polymer shell allowing the coupling of a large variety of enzymes, antibodies, antigens, polypeptides, proteins, *etc*. Thus, these bio-compatibilized magnetic nanoparticles can be used *in vitro* and *in vivo* systems for applications such as separation of molecules or cells, targeting of drugs, immunoassays, hybridization assays, biochemical or enzymatic reactions, affinity chromatography *etc*.

Another field of interest concerns the hybrid pigments used in the manufacture of cosmetics, inks and paints. Concerning these latter water paints are of paramount interest for environmental reasons. Light scattering power and hiding coverage of the paint are optimal if the nanoparticle pigments are uniformly spaced apart an ideal distance. The encapsulation of inorganic hydrophilic pigment particles with polymer will improve their compatibility with the organophilic polymer binder and therefore agglomeration can be prevented. Thus film paint appearance and performances such as higher gloss, better scrub resistance and adhesion, hiding power, water vapor permeability, storage stability, flexural strength, color stability and durability can be improved.

For example in such a domain, Caris developed a smart method for polymerizing MMA at the surface of submicronic titania particles.[256] The inorganic particles were modified with titanate alkoxo carboxylate coupling agents such as $Ti(OPr^i)_2(OCO–CH_2–C_{16}H_{33})(OCO–methacrylate)$. The titanate reacts with the hydroxyl groups present on the TiO_2 particle surface leading to modified titanium dioxide particles carrying $Ti–OCO–CH_2–C_{16}H_{33}$ and Ti–OCO–methacrylate hydrophobic groups. As a consequence these modified particles can be dispersed in a solution of sodium dodecyl sulfate in water, creating thus a micelle like structure with an inorganic particle in the center. In this system an emulsion polymerization of MMA was carried out; the materials obtained have core–shell morphology with a titania core and a polymer shell made of PMMA either covalently bonded to the titanate surface coupling agents by their methacrylate functions or physically bonded by entanglement.

This strategy could be easily extrapolated to non-aggregated nanosized particles (amorphous or crystalline) of some tetravalent oxides such as CeO_2, SnO_2 or ZrO_2.[257–260] Moreover these non-aggregated particles are generally surface protected by complexing ligands such as acetylacetonates or α-hydroxy acids. These complexing agents establish iono-covalent bonds resulting from a favorable equilibrium of complexation with the metallic atoms located at the particle surface. Consequently they could be conveniently exchanged with other complexing ligands. If these new ligands bear a polymerizable function such as methacrylate, pyrrole or thiophene they could be used as anchoring points to start polymerization reactions with free monomers. The polymerization should occur at the surface of the protected nanosized inorganic particles.

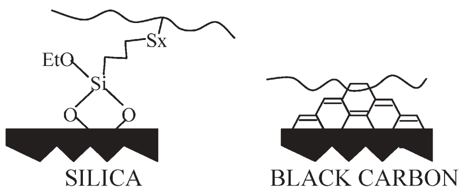


Fig. 24 Elastomer-charge bonding.

Among the real applications of hybrid NBB materials that are already on the market or will be in the short–medium term, the following ones can be underlined:

(i) Strathclyde University is currently developing intelligent packaging—able to tell the consumer how fresh a packet of meat or a pint of milk is—just by using nanoparticles that change colour if there has been any oxidation of the food inside the packaging. It works like an "oxygen intelligent" ink.

ii) Hybrid NBB nanocomposites are already used as nanofillers in the "Green Tyres"[261,262] developed by Michelin through a collaboration with Rhodia. The rolling bands are constituted by elastomer (rubber) containing nanosilica particles fillers. A good compatibilisation between the inorganic nano-filler and the rubber is achieved *via* the hybridisation of the nanosilica surface with organosilane coupling agents carrying di-sulfur functionalities that can bond chemically to the elastomeric network (see Fig. 24). The nanosilica replaces the conventional carbon black allowing improvement of aesthetic because these tyres can be colored. Thus, the resulting new tyres have a low rolling resistance maintaining the same adherence and durability properties and with access to any type of coloration. Moreover, this kind of tyre has been coined "green tyre" as it reduces the fuel consumption by 5%, contributing to a minor carbonic gas release to the atmosphere.

iii) Hybrid NBB coatings are also used in art conservation. One of the most striking examples concerns the long term protection of the 14th century "Last Judgment Mosaic" situated above the gates of the St Vitus cathedral in Prague castle.[104] The selected coating for treatment of the entire 13 m × 10 m mosaic is a multilayer system composed of a hybrid organic–inorganic functional layer made from organo alkoxysilanes and oxide nanoparticles, placed between the multicolored glass substrate and a fluoropolymer coating (see Fig. 25). This coating combination is a transparent efficient anti-corrosion barrier, much better than all tested organic polymers.[104]

III.4.b. Hybrids obtained by intercalation of organic components in 2D solids. From the pioneering works of Blumstein in

Fig. 25 Last Judgment Mosaic in Prague is a large outdoor panel made from 1 million multicolored glass tiles, or tesserae, embedded in mortar. This high potassium glass is chemically unstable and since the glass is exposed to harsh weather conditions (high SO_2 levels, rain, temperatures varying from -30 °C to $+65$ °C), the alkali reacts with the atmosphere and water from salt deposits that burrs and corrodes the masterpiece. All organic polymers used in previous protection attempts have failed to stop corrosion, because of their poor durability, poor adhesion to the glass, and large diffusion coefficient for SO_2 and water. After reviewing many possible choices the most efficient coating was made from a combination of a hybrid nanocomposite and a fuoropolymer [Copyright Getty Conservation Institute, Photograph Jaroslav Zastoupil (Courtesy of Eric Bescher[104])].

1961,[263] showing the ability of neutral unsaturated monomers (acrylonitrile, methyl methacrylate and vinyl acetate) to intercalate into montmorillonite, to the present the study of intercalation of organic components into different inorganic 2D host lattices has been very intense.[264–267] The progress in the development of organically modified 2D nanocomposites is summarized in Table 4 (adapted from reference 268).

Organically modified-2D nanocomposites present numerous applications according to their structural and/or functional properties. The first ones result from combinations of polymers whose interest is centered on their mechanical or rheological properties, such as nylon–clay nanocomposites,[266,290–292] whereas the latter ones refer to nanostructured materials with specific chemical or physical properties such as for instance the case of conducting nanocomposites,[293] and more recently bio-inspired materials.[268,294]

Depending on the nature of the 2D host and guest polymer, several successful procedures can be followed to enable the controlled incorporation of organic functions into an inorganic solid: intercalation, grafting, and molecular assembling.

The insertion of organic species inside the layers of inorganic lamellar solids was firstly achieved in phyllosilicates such as montmorillonite, which is a smectite clay mineral, however, in addition to clay minerals, other 2D solids having different chemical compositions, such as alkaline-silicates, titanates, niobates, molybdates, and phosphates with a layered structure

Table 4 Chronological development of organically modified 2D nanocomposites (adapted from reference 268)

Year	Organic–inorganic hybrid	Examples	Authors and references
1939	Clay minerals intercalated by organic cations	Montmorillonite/quaternary ammonium species	Gieseking[269]
1948	Clay minerals intercalated by neutral species	Montmorillonite/neutral polar molecules	MacEwan[270]
1959	Graphite oxide (GO) intercalation compounds	GO/alkylamines	Aragón *et al.*[271]
1961	Polymer–clay intercalation compounds	Montmorillonite/polyacrylonitrile	Blumstein[263]
1965	Layered phosphate intercalation compounds	α-$[Zr(PO_4)_2H_2]\cdot H_2O$/alkylamines	Michel and Weiss[272]
1967	Transition metal oxychloride intercalation compounds	FeOCl/amines	Hagenmuller *et al.*[273]
1969	Transition metal dichalcogenide intercalation compounds	TiS_2/amines	Weiss and Ruthard[274]
1973	LDH intercalated by organic anions	$[Zn_3Al(OH)_8]$/dicarboxylates	Miyata and Kumora[275]
1964–1968	Organic derivatives of silicates	Organosilanes grafted on olivine, chrysotile, *etc.*	Lentz,[276] Fripiat and Mendelovici[277]
1976–1978	Organic derivatives of layered phosphates	Grafting of epoxidesand direct synthesis of organophosphonates in α-Zr phosphate	Yamanaka,[278] Alberti *et al.*[279]
1979	Intercalation compounds based on layered silicic acids	Magadiite/alkylamines	Lagaly[280]
1980	Organic derivatives of layered silicic acids	Interlamellar grafting of trimethylsilyl groups on H-magadiite	Ruiz-Hitzky and Rojo[281]
1986	Conducting polymer–2D intercalated materials	FeOCl/polypyrrole	Kanatzidis *et al.*[282]
1987	Clay intercalated by polymer	Montmorillonite/6-polyamide	Fukushima and Inagaki[283]
1990–1992	Ion conducting polymer–2D intercalated materials	PEG and PEO/phyllosilicates	Ruiz-Hitzky and Aranda[284,285]
1991–1992	Organic derivatives of layered transition metal oxides	PEO/layered V_2O_5	Liu *et al.*,[286] Ruiz-Hiztky *et al.*[287]
2000	Bio-organic derivatives of LDH	ADN/LDH	Choy *et al.*[288]
2002	Macrocycles/clay "hybrid organic–inorganic liposomes" (HOIL)	Montmorillonite–crown ether/polybutadiene composite membrane	Ruiz-Hitzky *et al.*[289]

can act as cation exchangers to produce very stable intercalation complexes. The intercalation of alkyl- and arylammonium, protonated nitrogenated bases, amino acids, and complex cations such as cationic dyes, bioactive charged species or polyelectrolytes in smectites has been extensively investigated.[264] In particular, Ogawa and Kuroda have published a well-focused review on organo-ammonium intercalation in layered silicates, discussing the most salient properties and potential applications derived from this type of hybrid organic–inorganic material.[295]

Unlike the above mentioned solids, hydrotalcite-like materials (layered double hydroxides, or LDHs) intercalate anionic species, such as organic sulfates, sulfonates, phosphates, carboxylates or anionic surfactants (*e.g.* dodecylsulfonates). Organic compounds, including polymers, of interest for their photoactive, conductive or biological behaviour have been reported as suitable species to form functional LDH based materials.[296,297]

Numerous groups are interested in the preparation of hybrid multifunctional and bioinspired materials which are able to entrap active molecular species and which can immobilize diverse biomolecules such as proteins, enzymes, antigens, DNA, RNA, *etc.*, for gene therapy. In this sense, Choy *et al.* have verified the efficacy of LDH systems for encapsulating DNA acting as nonviral vectors in the treatment of cancer.[288]

III.4.c. Hybrid nanocomposites based on clays. Due to the great importance of clay-derived nanocomposites (see Fig. 3, Path B2) and, in particular, polymer–clay nanocomposites in the industrial market, a separate chapter must be included for them. They comprise organic/inorganic hybrid polymer matrices containing platelet-shaped clay particles that have sizes on the order of a few nanometers in thickness and several hundred nanometers in length. In relation to the unmodified polymer, the polymer/clay may exhibit drastic improvements in strength, modulus, and toughness; tear, radiation, and fire resistance; and lower thermal expansion and permeability to gases while retaining a high degree of optical transparency.[298,299]

Many clays are layered aluminosilicates, which present a sheet-like structure (typically, silica SiO_4 tetrahedra bonded to alumina AlO_6 octahedra) with charge-compensating counterions (such as Li^+, Na^+, K^+, Ca^+, *etc.*) located in the inter-layer space.[300] One important consequence of the charged nature of the clays is that they are generally hydrophilic species and therefore incompatible with a wide range of polymer types. In order to enhance compatibility with organophilic polymers, the alkali or alkaline-earth interlayer cations are replaced by means of ion exchange reactions with organic ammonium and phosphonium cations.[301,302] These organic cations diminish the surface energy of the inorganic components and improve the wetting characteristics with the polymer. This treatment leads to organically modified layered silicates, namely organoclays (OC). Other types of clay modifications can be used depending on the choice of polymer (epoxy resin, nylon, polycaprolactone, polyurethane, *etc.*), including ion–dipole interactions, use of silane coupling agents and use of block copolymers (SBS, SEBS, PEO-PPO-PEO, *etc.*).[303]

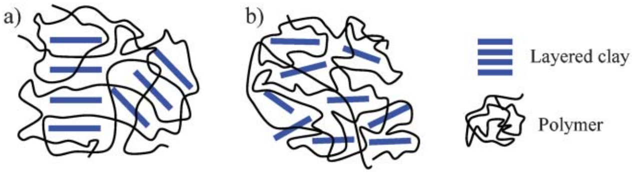


Fig. 26 Scheme of the (a) intercalated and (b) exfoliated polymer–clay nanocomposites.

The aim of the polymer layered silicate nanocomposite fabrication is to uniformly disperse and distribute the inorganic components, initially composed of aggregates of stacks of parallel layers, within the polymer, and avoid the formation of traditional filled polymers with less applications.

The compatibility between organic polymers and inorganic hosts results in systems exhibiting *intercalated* or *exfoliated* morphology, as represented in Fig. 26.

In the intercalated structure, the organic component is inserted between the layers of the clay in such way that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. In an exfoliated structure, the layers of the clay have been completely separated and the individual layers are distributed throughout the organic matrix.

Since the type of delamination determines the properties of the clay nanocomposites, several factors such as the exchange capacity of the clay, the polarity of the reaction medium and the chemical nature of the interlayer cations must be taken into account for the synthesis of the polymer–clay hybrids.

The synthetic route of choice for making a nanocomposite depends on whether the final material is required in the form of an intercalated or exfoliated hybrid, but in general, four approaches have been developed:[298] (i) *solution processing*, in which a common solvent is used to disperse the organically modified-clay as well as the polymer, (ii) *mesophase mediated processing*, that involves a two-phase reaction medium (emulsion, suspension polymerization, *etc.*) in which the silicate layers are suspended in an aqueous phase and a monomer is polymerized in a second phase within the suspension; (iii) *in situ polymerization*, whereby the monomer is used directly as the solubilizing agent for the organoclay; and (iv) *melt processing*, in which the clay and the polymer melt are mixed statically or under shear.

Organo-clays receive great interest for applications based on their capacity for selective adsorption of molecules. Thus, they have been used for application in chromatography separations,[304] to remove organic pollutants from air and water, and to develop improved formulation for pesticides,[305] as chemical sensor and molecular sieves,[306] *etc.*

Some examples of commercial applications. The control and manipulation of nano-sized clay particles is viewed as crucial for the creation of smart materials, by combining the wide type of properties provided by the clay with the functionality of organic components. Despite the enormous potential applications of these nanocomposites, their commercialization has been delayed due to the significant costs and difficulty in dispersing the nano-sized clay layers within the polymer at the industrial scale. However, research in the commercial realization has allowed the development of real smart nanomaterials.[298,307,308] Some of the most striking commercial successes are illustrated as follows.

a) Clay-polymer nanocomposites with structural properties. The first successful development of clay–polymer nanocomposites was pioneered by Toyota's researchers Inagaki *et al.*[309,310] for structural applications in vehicles. They prepared a clay–nylon nanocomposite through the *in situ polymerization* method, in which ADA-modified clay was dispersed in the monomer caprolactam, further polymerized to form the nylon-6–clay hybrid as an exfoliated composite. Efforts within the last 10 years have demonstrated a doubling in tensile modulus and strength without sacrificing impact resistance for nylon-layer silicate nanocomposites containing as little as 2 vol% inorganics.

Earliest successes in the automotive industry are possible thanks to the sonication process developed by Ford Corporation to better disperse the clay within the polymer. From this processing, General Motors Corporation (GMC) developed a step-assist[311] (see Fig. 27) for 2002 Safari (GMC) and Astro (Chevrolet) vans, which are made of a nanocomposite based on clay and a thermoplastic olefin. This material is not only lighter in weight and stiffer, but also more robust at low temperatures and more recyclable. GMC also used these nanocomposites in the lateral protection wires of the 2004 model Impala Chevrolet[312] since they are 7% lighter in weight and present a better surface state (see Fig. 27).

New applications of hybrid nano-clay materials are nowadays envisaged by automotive industrials for a next commercialization: PP/clays for bodywork with anti-scratch properties (Dow Plastics/Magma); acetal/clays for ceiling-lights (Showa Denko); PP/clays for panes of doors, consoles and interior decoration (Ford, Volvo) due to aesthetics, recyclable and lightness properties, nylon/clays for bumpers with enhanced mechanical and lightness properties (Toyota), nylon/clays for fuel reservoir with airtightness properties (Ube America), *etc.*

Besides these properties, the weight advantage could present a significant impact on environmental concerns. For example, it has been reported[313] that widespread use of PNCs by U.S. vehicle manufacturers could save 1.5 billion litres of gasoline in one year of vehicle production and reduce related carbon dioxide emissions by more than 10 billion pounds.

In relation to the environmental applications, organically-modified nanoclays are used as effective reinforcement agents in the so-called "green" nanocomposites.[314] These renewable-resource-base biodegradable nanocomposites are based on cellulosic plastic (plastic made from wood), polylactic acid (corn-derived plastic) or polyhydroxyalkanoate (bacterial polyesters) and they are attractive as a substitute for petroleum feedstock in making plastic in the commercial market.[315]

Fig. 27 Two of the first commercial applications of clay-based nanocomposites in the automobile industry: (left) the step-assist and (right) lateral protection wires.

b) Clay–polymer nanocomposites with gas barrier properties. By incorporation of nanosized clays in polymer matrices, it is possible to create a form of labyrinth within the structure, which physically delays the passage of molecules of, *e.g.*, gas. The excellent barrier properties against gas and vapour transmission have resulted in applications mainly for food and beverage packaging, as well as for barrier liners in storage tanks and fuel lines for cryogenic fuels in aerospace systems.[316]

In particular, the market involved in clay–polymer nanocomposites for food packaging have experimented an enormous development in the recent years. Specific examples include packaging for processed meats, cheese, confectionery, cereals and boil-in-the-bag foods, 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.

In the food packaging, only two plastics were available in the past to protect the food from moisture and oxygen: inexpensive but somewhat more permeable polyamide 6 for less sensitive foods, and expensive but more airtight ethylene vinyl alcohol (EVOH) for sensitive products. Researchers at Bayer Polymers have developed a hybrid material including silicate nanoparticles with advantages of both plastics: it is inexpensive, but still very airtight, not as good as EVOH, but much better than simple polyamide 6.[317]

Nanocor and Mitsubishi Gas Chemical Company developed the MXD6 high barrier semi-aromatic nylons in nanocomposite form.[318] Mitsubishi was among the leading pioneers in shelf-life extension, but in nanocomposite form, marketed under the Imperm® trade name, a new material features oxygen and carbon dioxide barrier properties that were previously unachievable. Its barrier properties are said to make Imperm® superior to EVOH and its processing characteristics are ideal for multilayer films, bottles and thermoformed containers (see Fig. 28).

Honeywell (Virginy, Southern Caroline) has developed a polyamide-based nanocomposite with specific active and passive barrier properties against oxygen.[317] The passive barriers are the clay particles, which render more difficult the oxygen transmission inside the composite, but they also

Fig. 28 Mitsubishi super gas barrier nylon.[318]

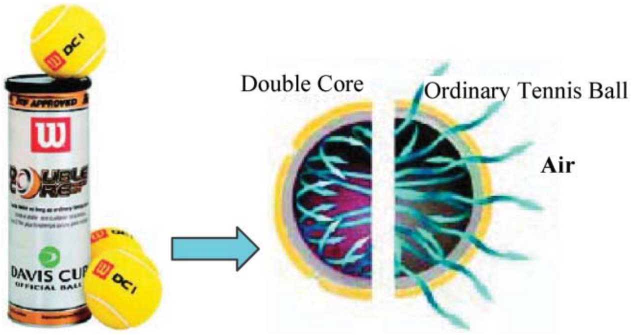


Fig. 29 The core of this commercial tennis ball is covered by a polymer–clay nanocomposite coating that acts as a gas barrier, doubling its shelf-life.

conduct the oxygen molecules to specific oxygen-captors (active contribution). In this way, the clay incorporation limits the oxygen transmission up to 15–20% of the value found for the pure polymer.

Triton Systems and the US Army work together on nanoclay–polymer nanocomposites as non-refrigerated package materials, which can conserve food freshness for three years.[319]

InMat Inc. has developed several applications for their nanocomposite coatings, especially in tennis balls, that conserve the internal pressure for a long time.[301a,320] Fig. 29 shows the Wilson tennis balls, provided with a double core.

The core is covered by a polymer–clay (vermiculite) nanocomposite coating that acts as a gas barrier, doubling its shelf-life. This technology could be extended to the rubber industry, since it is too permeable for certain applications, and it could be incorporated in footballs or in tyres of bicycles, cars or trucks.

The barrier properties of clay–polymer nanocomposites have also been extended to liquids (solvents) or molecules such as water, since they produce a faster aging of the polymers. The ability of nanoclay incorporation to reduce solvent transmission in polymers has been demonstrated. For example, De Bievre and Nakamura of UBE Industries reveals significant reduction in fuel transmission through polyamide-6/66 polymers by incorporation of nanoclay filler, resulting in a considerable interest for fuel tanks and fuel line components.[317c] In the case of barrier nanocomposites against water, it has been observed that its absorption or diffusion is related to the morphology of the clay layers: the higher the length/thickness ratio, the lower is the water absorption.

In the same research line, InMat Inc. collaborates with the US Army in the concept of barriers against liquids and hydrocarbons.[321] Some envisaged applications are protective gloves and coatings for combustible and fuel tanks.

c) Clay–polymer nanocomposites with antiflammability properties. Thermal stability and fire retardancy have motivated investigation of PLSNs as a component in antiflammability additives for commodity polymers.[322]

As fireproof polymers, silicate–polymer nanocomposites present a crucial advantage: the low loading of clays (typically 2–5%), in contrast to up to 60% of additives in classical fire-resistant polymers. This is explained by the formation of a superficial insulating char coating, which not only delays the polymer degradation but also diminishes the calorific power.[299]

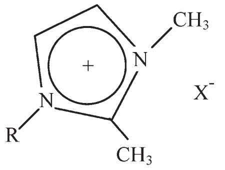


Fig. 30 Structure of an imidazolium salt.

Gitto (polymer maker) and Nanocor (clay manufacturer) have developed a joint program to obtain fireproof polyolefins by incorporation of clay nanoparticles, since this polymer has a wide range of industrial applications.[323]

On the other hand, the heat-distortion temperature of these nanocomposites can be increased by up to 100 °C, extending their use to higher temperature environments, such as under-the-hood parts in automobiles.

For preparation of nanocomposites from high temperature engineering thermoplastics, the major limitation in the use of conventional counter-ion modified clays is the thermal instability of the alkylammonium species during processing. A block copolymer route developed by TNO (Netherlands), in which one component of the copolymer is compatible with the clay and the other with the polymer matrix, offers one potential solution to this problem.[301a] Imidazolium salts such as that depicted in Fig. 30 are also more thermally stable than the ammonium salts.

A further alternative is the use of phosphonium salts that can lead to an increase in the degradation temperature from 200–300 °C to >300 °C. Wholly synthetic OLS can exhibit thermal stability of beyond 400 °C. By using these last two approaches, Triton Systems[319] have succeeded in producing nanocomposites from high temperature resins such as polyetherimide (PEI).

d) Clay–polymer nanocomposites with other properties. In some cases, the value of the clay–polymer nanocomposites technology is based less on pure mechanical, barrier properties or fireproof enhancements than on the so-called value-added properties not present in the neat resin but arising from low volume additions of the OLS. For example, in contrast to conventional filled resins, which are opaque, low volume-fraction additions and nanoscopic dimensions of the dispersed organically modified layered silicate result in nanocomposites with optical transparency, comparable to the base resin. Moreover, depending on the type of polymeric host, they can also display interesting ionic conductivity for solid-state electrolytes in batteries[324,325] or in thermal expansion control.[326]

Some indications about the nanocomposites world market. According to a report of the Business Communication Co. Inc., the world market of hybrid clay–polymer nanocomposites involved 11.123 tons and US$ 90.8 million in 2003. With the estimated increase of 18.4%, this market will represent 36.000 tons and US$ 211 million by 2008. Fig. 31 gives an

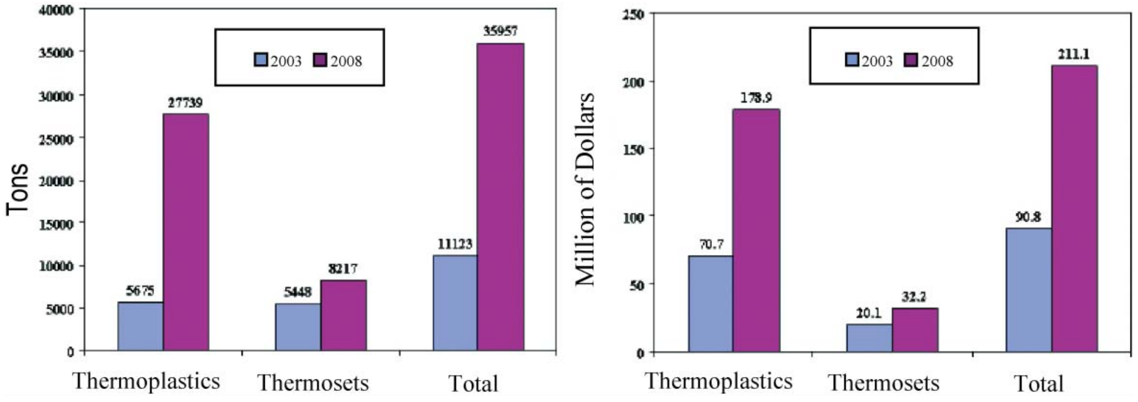


Fig. 31 World production of polymer nanocomposites.

Table 5 List of some nanocomposites suppliers[307a]

Supplier	Matrix resin	Nano-filler	Target market
Bayer AG	Nylon 6	Clay	Barrier films
Clariant	Polypropylene	Clay	Packaging
Creanova	Nylon 12	Nano-tubes	Electrically conductive
GE Plastics	PPO/Nylon	Nano-tubes	Painted automobile parts
Honeywell	Nylon 6	Clay	Films and bottles
Hyperion	PETG, PBT, PPS, PC, PP	Nano-tubes	Electrically conductive
Kabelwerk Eupen of Belgium	EVA	Clay	Wires and cables
Nanocor	Nylon 6, PP, Nylon MDX6	Clay	Beer bottles, molding
Polymeric Supply	Unsaturated polyester	Clay	Marine, transportation
RTP	Nylon 6, PP	Clay	Electrically conductive
Showa Denko	Nylon 6, Acetal	Clay, mica	Flame retardance
Ube	Nylon 6, 12, 66	Clay	Auto fuel systems
Yantai Haili Ind. & Commerce of China	UHMWPE	Clay	Earthquake-resistance pipes

indication of how the world production of nanocomposites is progressing in the short–medium term.[307,308]

Even if the thermoplastics and thermosets production is nowadays similar in volume, the total commercial value of thermoplastics is 3.5 times more important (Fig. 31). Therefore, the estimation for 2008 is that thermoplastics should represent 77% of the production in volume and 85% in commercial value. As remarkable data: General Motors Corporation consumes around 245 tons of these nanocomposites per year, most of them based on olefins; and BRG Townsend Inc. (package industry) estimated in 2002 that its nanocomposites consumption intended for 2007 should be 2200 tons per year and 45000 tons in 2011.

Nanocomposites represent an important part of the activities in great companies such as Bayer, GE or Honeywell, as well as in more specialized enterprises. In Table 5 the wide range of resins used at the present time for polymer–clay nanocomposites is summarized. A new generation of synthetic nanomaterials as nanotubes or ceramic nanofibers are also emerging, but these smart materials are at least five to ten years away from commercial realisation.

IV. Conclusions

Looking to the 21st century, nanosciences will be one of the fields that will contribute to a high level of scientific and technological developments. Hybrid organic–(bio)–inorganic materials will play a major role in the development of advanced functional materials.

Research in functional hybrid organic–inorganic materials is being mostly supported by the growing interest of chemists, physicists, biologists and materials scientists to fully exploit this opportunity for creating smart materials benefiting from the best of the three realms: inorganic, organic and biological. Even bio-inspired strategies are used to "mimic" the growth processes occurring in biomineralization and design innovative multiscale structured hybrids (from nano- to millimetric scale), hierarchically organized in terms of structure and functions.

In addition to the high versatility in chemical and physical properties and shaping, hybrid nanocomposites present the paramount advantage to both facilitate integration and miniaturization, therefore opening a land of promising applications in many fields: optics, electronics, ionics, mechanics, membranes, functional and protective coatings, catalysis, sensors, biology, medicine, biotechnology, *etc.*

During the past decade, many hybrid materials have been appearing either as prototype or commercial products. Several examples of "commercial hybrids" have been discussed in this review but they only represent a small fraction of the tip of the iceberg.

Nowadays molecular approaches of solid state chemistry and nanochemistry have reached a very high level of sophistication. Chemists can practically tailor-make any molecular species (molecules, clusters, nanosized particles, nanolamellar compounds, nanotubes, *etc.*) and design new functional hybrid materials with enhanced properties.

At this level of knowledge and understanding in nanoscience, and bearing in mind the new and stricter requirements imposed by the current society, manufacture of intelligent materials and devices with complex structures, high level of integration and miniaturisation, recyclable and respecting the environment, is just a question of scientist's imagination and of making industrys aware of their opportunities and benefits. In this context, we bet that advanced hybrid materials will play a major role.

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