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On Form Dictating Function: Shape and Structural Effects in Silica-based Funtional Materials

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ABSTRACT: Along with basic physicochemical properties, the morphology of sol-gel materials, both on the macro-, meso-, and nanoscale, controls function and utility. Referring to recent achievements, we focus on the relation between form and activity for functional silica-based materials to elucidate a few general concepts of usefulness in guiding research in this burgeoning field.
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1. Introduction and Background

Large efforts in contemporary research in materials science and biology are being aimed at preparing materials with functionally powerful shapes based on the understanding of the constructional processes that give rise to complex inorganic structures under the mild, wet conditions typical of biological processes. One general finding of these studies is that porosity is a fundamental part of any nanostructured material that does chemistry, as the void phase ensures both accessibility, dispersion, and effective confinement of any entrapped molecules.[1] To paraphrase Davis,[2] beyond the atoms and molecules that define the porous space, the challenge in the field of porous materials aims to control their shape. In other words, void space and deliberate disorder are used as design components, as disorder and geometrical imperfection of solid structures have long been known for their unique relevance to heterogeneous chemical processes.[3] Eventually, the overall objective is to develop what has been called "a chemistry of form"[4] in the laboratory.

Silica-based materials obtained by the sol-gel process are perhaps the most promising class of functional materials capable of meeting such a grand objective. In the sol-gel process, liquid precursors such as silicon alkoxides, are mixed and transformed into silica through hydrolytic polycondensation at room temperature.[5] Called "soft chemistry" or "chimie douce"[6], this approach to the synthesis of glasses at room temperature and pressure and in biocompatible conditions (water, neutral pH) has been pioneered by Livage and Rouxel in the 1970s, and further developed by Sanchez, Avnir, Brinker, and Ozin.

These and several other researchers extended the methodology with the aim to widen functionality, using dopant molecules and silicon precursors derivatized with organic moities giving place to a vast class of hybrid organic-inorganic organosilica nanocomposites capable to meet numerous advanced requirements in fields as diverse as catalysis, chromatography, surface coating, sensing, drug release, and biotechnology.[7]

In general, from Ozin's periodic mesoporous organosilicas (PMO)[8] to Brinker's evaporation-induced self-assembly (EISA),[9] sol-gel processing is coupled to molecular self-assembly as a simple, general means to prepare porous and composite nanostructures. Hence, by generalizing into chemistry the biominerals growth principles, elucidated in the late 1910s,[10] one may recognize how organics, and especially soft matter (lyotopic mesophases, foams, emulsions, and beyond),[11] are used to template all types of porous materials (Scheme 1).

This emerging approach to functional materials has been named by Ozin "nanochemistry",[12] and refers to a basic chemical strategy for making nanomaterials using molecular or nanometer scale building blocks (with a wide range of shapes, compositions, and surface functionalities) that are further

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small organic molecules → microporous (Fick diffusion of molecules only: high reactivity)

micelles, liquid-crystals, block-copolymers → mesoporous (fluid that flow in which molecules are diffusing, this is called a depletion phenomenon: accessibility and reactivity)

microemulsions → macroporous (above 50 nm, imbibition of the fluid driven by the Darcy’s law: high accessibility)

Scheme 1. Organic templates controlling the porosity of materials (and consequences from a functional, reactivity viewpoint).

chemically processed to organize into structures serving as tailored functional materials. Indeed, solid state synthesis strategies in materials preparation are rapidly being supplanted by molecular methodologies, particularly the self-assembly of materials[13] with structures that mimic the complexity of those observed in nature.[14,15] Almost inevitably, then, concepts such as anisotropy or symmetry become key parameters when considering “form” effects on the chemistry of these functional materials.

As a general rule, the form of sol-gel materials, along with their basic chemistry and physics, controls function and utility. Now, in many fields of modern chemical research called to solve problems of great societal importance (from the elimination of byproducts and pollutants from chemical synthesis, to putting biological entities “at work” to produce the cornucopia of substances with the exquisite selectivity and efficiency found in nature), one finds that sol-gel silica-based oxides are actually playing a major role;[16] and, invariably, it is also found that the material’s architecture is of paramount importance. For example, wider bio-applications of sol-gel materials had to wait for bottom-up manipulation of the biogels affording powderless processing of shaped materials such as films or fibers.

We recently investigated the physical[17] and the chemical[18] effects of molecular sol-gel entrapment in silica-based materials. Now, referring to the recent development of complex shapes, such as silica nanotubes, fibers, thin-films, and Janus particles, we focus on the third functionally relevant aspect, namely morphology. We show how bottom-up nanochemical control over different levels of space organization is practically achieved to afford a variety of powerful functional silica-based materials in which shape indeed controls function and utility.

2. Confinement: Cage Morphology Dictating Chemistry

In general, the solid surface in molecularly doped organic-inorganic silica gels participates actively in the reaction mechanism, by: dictating access to the entrapped active molecule; providing a confined nanoenvironment that strongly differs from that experienced in solution; and reciprocally isolating and stabilizing the entrapped molecules. Control over the material’s shape at the nanoscale enables further control over the reactants access to the dopant, and ultimately affords a potent means of controlling function which is analogous to that parsimoniously employed by nature to synthesize materials with a myriad of functions with a surprisingly low number of material building blocks.

As mentioned above, surfactant templates enable the shape synthesis of mesostructured silica-based materials which represent an intermediate form of chemical control of matter. When the hydrolytic polycondensation of the alkoxide $Si(OR)_4$ is carried out in the presence of mesoscale (2–50 nm) micelle or macroscale (50–3000 nm) microsphere templates, self-assembly of periodic mesoporous and macroporous siliceous materials takes place. By changing the composition of the channel and the contents of the mesopore, one can adopt a rational strategy to functionalize mesoporous silicas; and this bottom-up approach has been the central synthetic strategy to make silica-based nanomaterials actually emerge since the discovery of mesoporous silica in 1990.[19]

A nice illustration is offered by the extrusion catalytic polymerization of ethylene within the hexagonal channels of MCM-41 mesoporous silica doped with catalyst titanocene.[20] The structure is made of amorphous silica walls spatially arranged into periodic arrays with high surface area (up to 1200 $m^2\ g^{-1}$) and mesopore volume >0.7 $mL\ g^{-1}$. In this case, restricted conformation dictates polymerization: the pore diameter (27 Å) is much smaller than the lamellar length of ordinary PE crystals (~100 Å), thus the PE chains are prevented from folding. In this manner, extended-chain crystalline nanofibers of linear polyethylene with an ultrahigh molecular weight (6,200,000) and a diameter of 30 to 50 nm are formed (Figure 1).

Order, however, is often detrimental to versatility. For example, cyclohexanol or long chain aliphatic alcohols, which simply cannot be aerobically oxidized over MCM-41 silicate

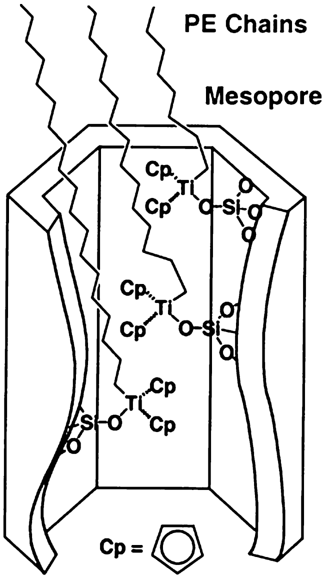


Figure 1. Extrusion polymerization on the nano scale. Schematic representation of the synthesis fibers of polyethylene within mesoporous silica channels doped with catalyst titanocene (reproduced from Ref. 20, with permission).

doped with perruthenate (Figure 2),[21] are instead smoothly converted into valued carbonyls over a methyl-modified silica xerogel doped with TPAP in which a large distribution of porosity allows access to the entrapped catalyst to widely different substrates.[22]

3. Symmetry: Chiral Objects and Chiral Cages Shaping Chemistry

Chiral silicas are chiral objects first obtained by Moreau in the early 2000s by transcription and self-assembly of bridged silsesquioxanes through cooperative weak interactions, affording chiral left- and right-handed organosilica helices[23] (Figure 3).

On the other hand, shaping the cages (voids) of amorphous silica xerogels by molecular imprinting results in shape-selective materials ideally suited for applications such as separations, chemical sensing, and catalysis.[24] For bulk silica, the method was first demonstrated by aminopropyl-modified silica acting as shape-selective basic catalysts.[25] The concept is general, and is now widely employed for producing selective imprinted xerogel sensors ideally suited for bioanalytical applications.[26]

A powerful extension of the imprinting concept is that of chirally imprinted sol-gel silicas allowing recognition that is based on chirality, and not on specific shapes. Here, a chiral surfactant [(1*R*,2*S*)-(−)-*N*-dodecyl-*N*-methylephedrinium bromide, for example] is used as a template resulting in an imprinted material with preferential adsorption of chiral solutes based on configuration matching between the cavity and the adsorbed molecule (Scheme 2).[27]

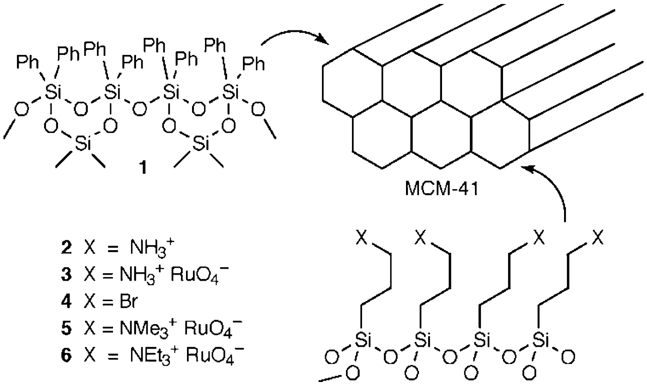


Figure 2. Entrapment of oxidation catalyst perruthenate inside the channels of MCM-41 silica results in a shape-selective aerobic catalyst, which may not be desirable from the viewpoint of catalytic versatility (reproduced from Ref. 21, with permission).

Chiral sol-gel thin films or bulk monoliths are thus obtained for the enantioselective adsorption and discrimination between pairs of enantiomers that are unrelated to the imprinting process. Remarkably, in order to enhance the intrinsic affinity of the surfactant to the silica matrix, the (−)-*N*-dodecyl-*N*-methylephedrinium bromide (DMB) cationic surfactant is entrapped in a 20%-phenylated silica in which it can also interact with the matrix through π-π interactions. This shows that to ensure optimal performance, one needs to exploit the versatile sol-gel chemistry to its full potential, addressing both the chemical and the morphological aspects of the sol-gel material.

4. Anisotropy and Dissymmetry: Silica Nanotubes and Janus Nanoparticles

Template synthesized silica nanotubes (SNTs) provide unique features, such as end functionalization to control drug release, inner voids for loading biomolecules, and distinctive inner and outer surfaces, that can be differentially functionalized for targeting and biocompatibility.[28] A general path to synthesize nanotubes utilizes anisotropic materials as a template. They are coated with silica using $Si(OR)_4$ precursors and nanotubes of SiO_2 are obtained after removal of the template (Figure 4).

Diverse chiral nanometric ribbons and tubules formed by self-assembly of organic amphiphilic molecules can be transcribed to inorganic nanostructures using a sol-gel transcription protocol with tetraethoxysilane (TEOS) in the absence of catalyst or cosolvent;[29] including open secondary architectures, rather than a closed tube, using tubules made of lipid

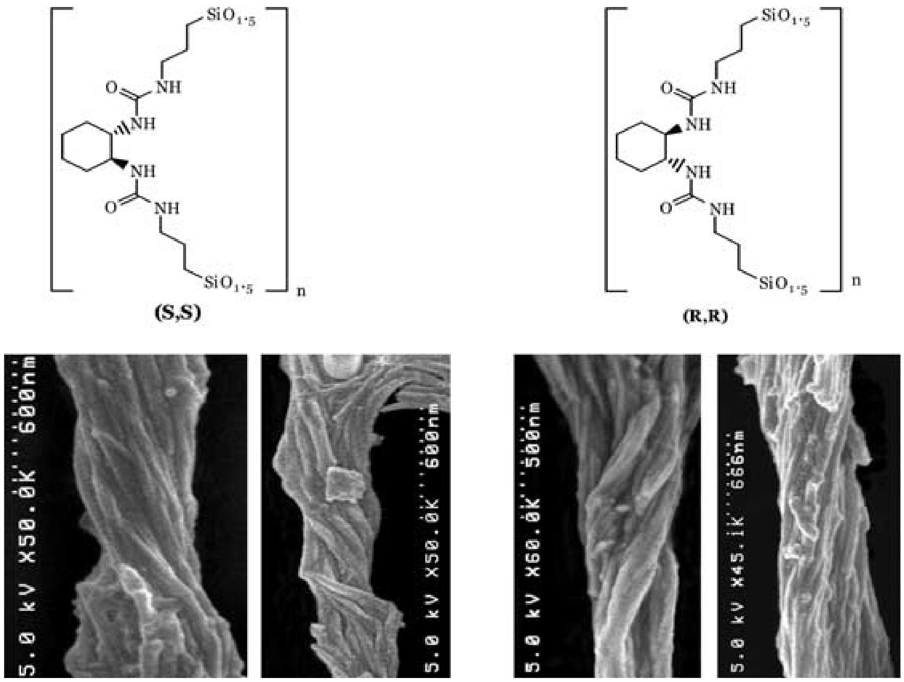
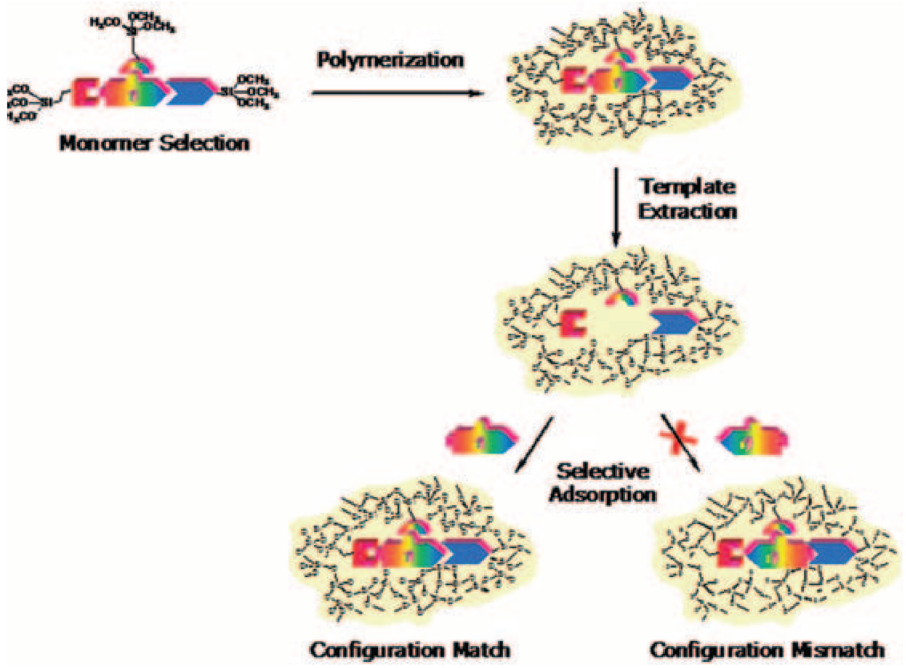


Figure 3. Helical hybrid silicas: chirality transcription from the precursor molecule to the hybrid solid (reproduced from Ref. 23, with permission).



Scheme 2. Formation of chiral cavity in a sol-gel matrix results in cages capable to discriminate enantiomers unrelated to the imprinting process (reproduced from Ref. 27, with permission).

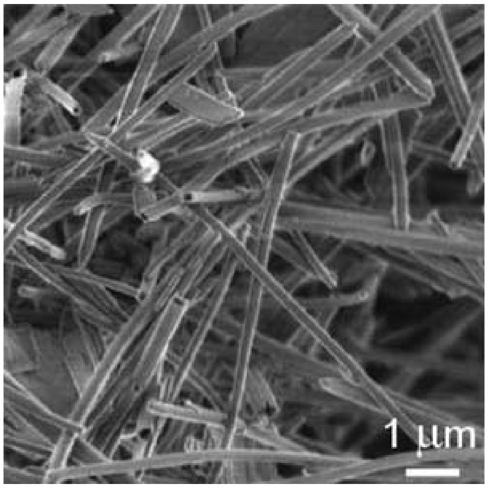


Figure 4. Silica nanotubes are formed by template synthesis using anisotropic materials ($V_3O_7 \cdot H_2O$, in this case) [reproduced from Ref. 28, with permission].

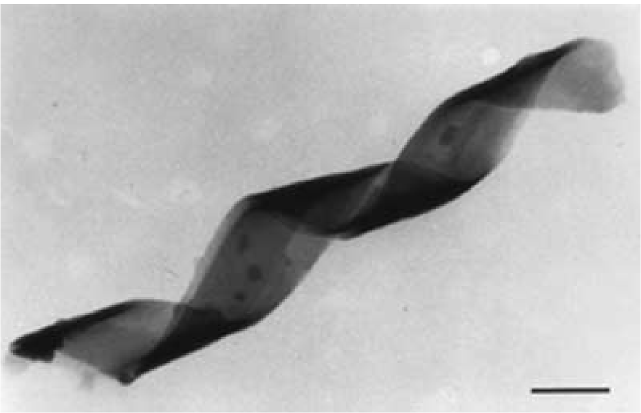


Figure 5. A silica–lipid mineralized helical ribbon (scale bar 400 nanometres) [reproduced from Ref. 30, with permission].

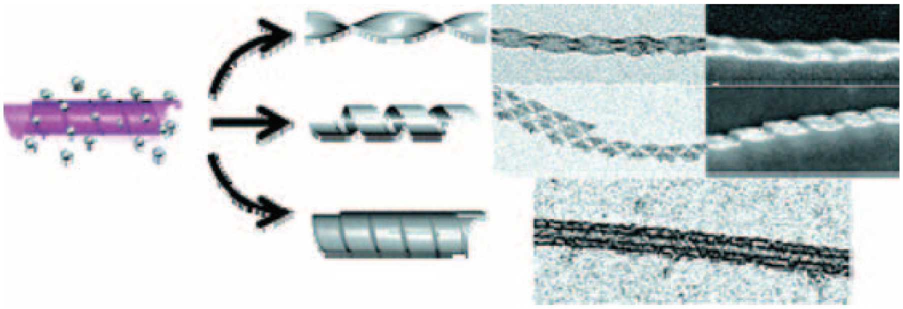


Figure 6. Template synthesis using organic gels expands the versatility of the methodology, affording largely different silica nanotubes (reproduced from Ref. 29, with permission).

surfactant ($DC_{8,9}PC$) that, once added to water containing TEOS, co-assemble with TEOS, hydrolyzing to produce silicate anions which interact with the lipid's cationic headgroups and deposit along the lipid bilayers as they twist into the helical shape (Figure 5).[30]

The dynamic and versatile nature of the organic gels considerably enhances the tunability of inorganic materials with rich polymorphisms (Figure 6), from nanotubes to nanohelices.

Hence, by controlling parameters such as temperature or the concentration of the different reactants, the morphology of the inorganic nanostructures formed from organic templates can be finely and widely tuned. Finally, long, double-walled glass nanotubes (fibers) ten times narrower than those currently available with a monodisperse diameter can now be easily synthesized using, as template, the synthetic peptide Lanreotide, that spontaneously self-assembles in water (5% w/w) forming 2 nm thick nanotubes with 24.4 nm diameter (Figure 7).[31]

Impressive, highly ordered centimeter-sized fibers are obtained whose synergistic growth mechanism based on the kinetic cross-coupling of a dynamic supramolecular self-assembly and a stabilizing silica mineralization may well be the basis of the synthetic paths used by nature to obtain materials with well-defined multiscale architectures in biological systems.

Called "Janus" particles by de Gennes,[32] with reference to the double-faced god of the Doors (Janus, in Latin), surface-dissymmetrical silica particles were discovered in the late 1980s.[33] Today, relatively large amounts of Janus nanoparticles (typically, one gram of Janus particles can be obtained within two days) can be synthesized in batch, based on the elegant concept that a removable mask can temporarily protect a part of an object in a reactive medium while a polymer nodule is grown onto the surface of silica particles to yield silica/polymer dissymmetrical colloids.[34] The unprotected mineral part of the resulting snowman-like particles is selectively functionalized and the protecting polymer mask is removed in a subsequent step (Scheme 3).

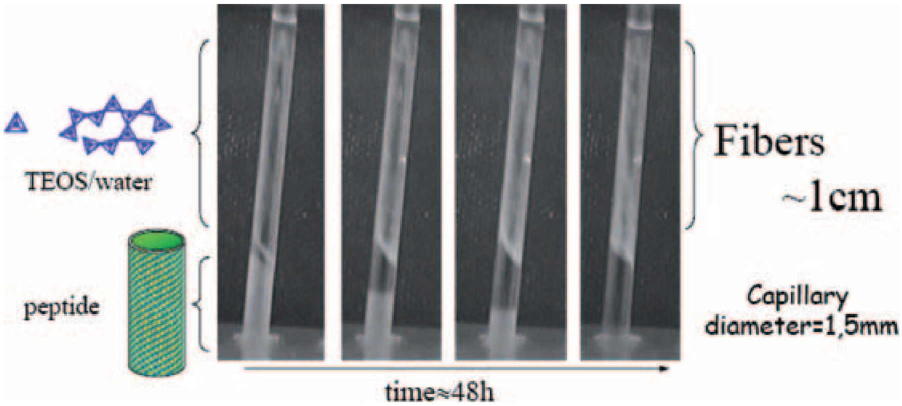
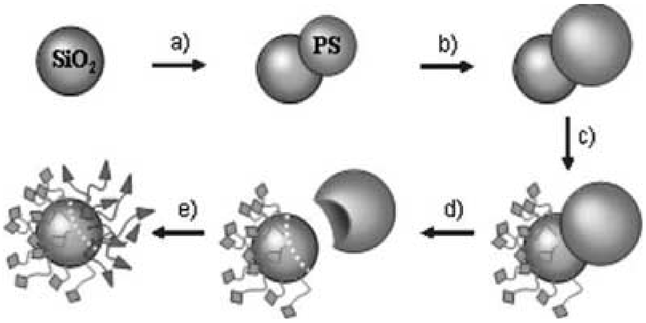


Figure 7. Double-walled silica nanotubes with monodisperse diameters self-organize into highly ordered centimetre-sized fibres, using a synthetic octapeptide as template. The growth mechanism is proposed to be the fundamental mechanism for growth processes in biological systems (reproduced from Ref. 31, with permission).



Scheme 3. Schematic representation of the consecutive stages for the fabrication of silica Janus nanoparticles (reproduced from Ref. 34, with permission).

The synthetic route for making the Janus nanoparticles first consists in the emulsion polymerization of styrene in the presence of silica nanoparticles surface-modified by polymerizable groups. Snowman-like hybrid nanostructures are thus obtained with 85% yield in which the chemisorbed polymer chains generated at the surface of the silica particles form one single nodule at the surface of the silica particle, as the high interfacial energy (owing to the presence of unreacted silanol groups) does not promote their spreading on the surface.

The specific functionalization of the unprotected silica surface with a trialkoxysilane derivative, such as $CH_3Si(OCH_3)_3$, is then carried out in a slightly basic water–ethanol suspension of the snowman-like particles. TEM images (Figure 8) of the resulting suspension of latex nanoparticles, whose unmodified part was further functionalized with a second trialkoxysilane, such as aminopropyltriethoxysilane, and then treated with an aqueous suspension of citrate-stabilized 18 nm gold nanoparticles, clearly show the dissymmetrical Janus character of the resulting latex particles by specific adsorption of the metal nanoparticles onto the amine-grafted mineral surface.

These nanostructures can be amphiphilic, bifluorescent, responsive to an electric field (with both hemispheres of opposite charges), and will be useful as biological and chemical sensors, stabilizers of complex media, and nanocomponents in smart displays.

5. Continuity: Thin Films

As a general trend in the application of sol-gel materials, traditional silicate monoliths and films are gradually giving way to thin permeable sol-gel films and microcapsules.[35] Continuous thin films, and not ill-defined powders formed by precipitation, are of interest for size-selective membranes, low dielectric constant insulators, sensors, and optical coatings. As self-assembly depends on the concentration of the two-sided surfactant molecules, Brinker developed the EISA concept,[9] namely evaporation-induced self-assembly, in which self assembly is induced by solvent evaporation to concentrate the evolving systems in surfactant and therefore drive the continuous formation of thin-film versions of these powders, including fast ink-jet printing[36] evaporative process.

A nice example is offered by the EISA one-pot preparation of ordered mesoporous functionalized silica thin films functionalized with silylated β-diketone compounds with controlled mesostructure, optical quality, and excellent cycling reproducibility and used for fast optical sensing of uranyl species with high selectivity and sensitivity (Figure 9). Mesostructured mesoporous thin films with their larger open porosity and their high surface area should improve analyte diffusion and accessibility towards supported probes. Moreover, both their monomodal narrow pore size distribution and their

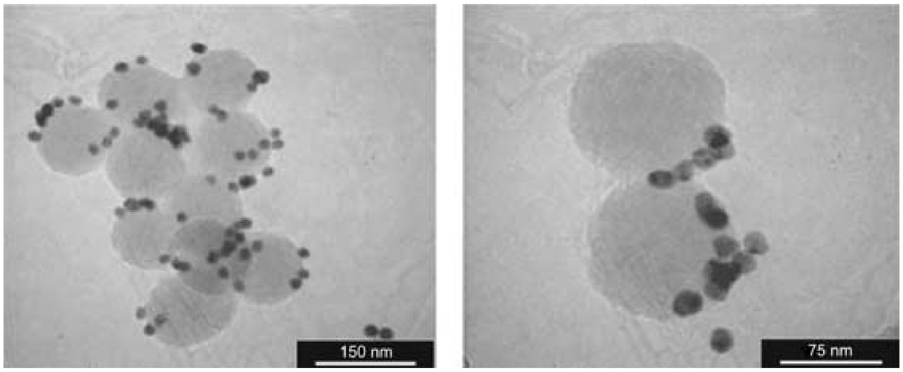


Figure 8. TEM images of Janus silica nanoparticles (diameter: 100 nm) in which the amine grafted area is decorated by gold nanocolloids, the remaining area being functionalized by methyl groups (reproduced from Ref. 34, with permission).

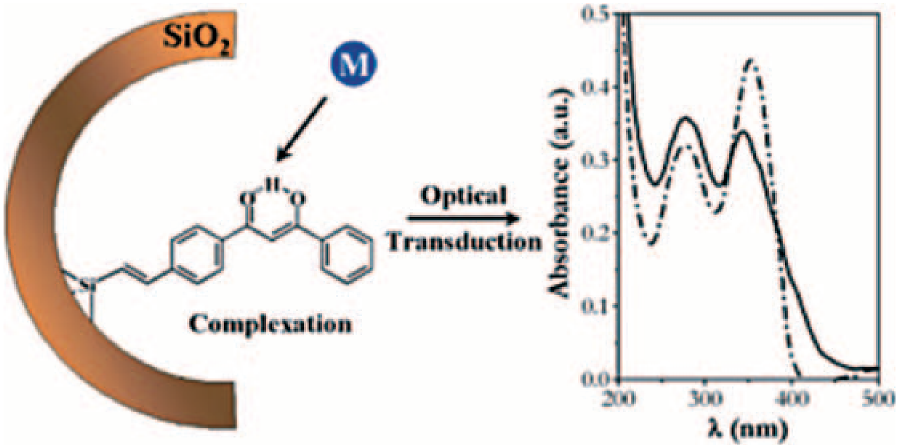


Figure 9. UV/Vis spectra of sensing layer before (dotted line) and after (solid line) immersion in a 100 ppm uranyl aqueous solution. Cation detection may be efficiently performed at 355 nm or 400 nm (reproduced from Ref. 37, with permission).

controlled porous connectivity makes them much more resistant to the huge capillary stresses usually arising from their instability and the collapsing of mesoporous xerogels during successive water dipping and drying sensing cycles.[37]

6. Hierarchy: Multifunctional Biohybrids

According to Brinker, to better emulate biology we need “to break symmetry and develop structure and function on a broader range of length scales”.[38] Remarkably, this is precisely what is being done through newly developed hierarchical hydrogel biohybrids. For example, simple monolithic bulks of biogels for catalytic purposes are often inappropriate. Indeed, an increase of the K_m (the concentration of substrate that leads to half-maximal velocity of the enzymatic reaction) for encapsulated enzymes as compared to that for the free protein in solution is generally observed, owing to resistance of the pores of the sol-gel matrix to the diffusion and transport of substrates to the enzyme.[39]

Mesoporous silica hydrogels processed into hierarchically organized structures are not affected by this limitation, offering a desirable combination of a high internal reactive surface along with narrow nanopores, with facile molecular transport through broad “highways” leading to (and from) these pores.[40] The biocompatibile self-assembly process used for their synthesis consists of unidirectional immersion of a hydrogel in liquid nitrogen (Figure 10).

The resulting ice-segregation induced self-assembly (ISISA) process proceeds in the absence of further chemical reactions. Ice formation (hexagonal form) causes every solute originally forming the hydrogel to segregate from the ice phase, giving rise to a macroporous structure characterized by fences of matter enclosing ice (Figure 11). The scaffolds obtained

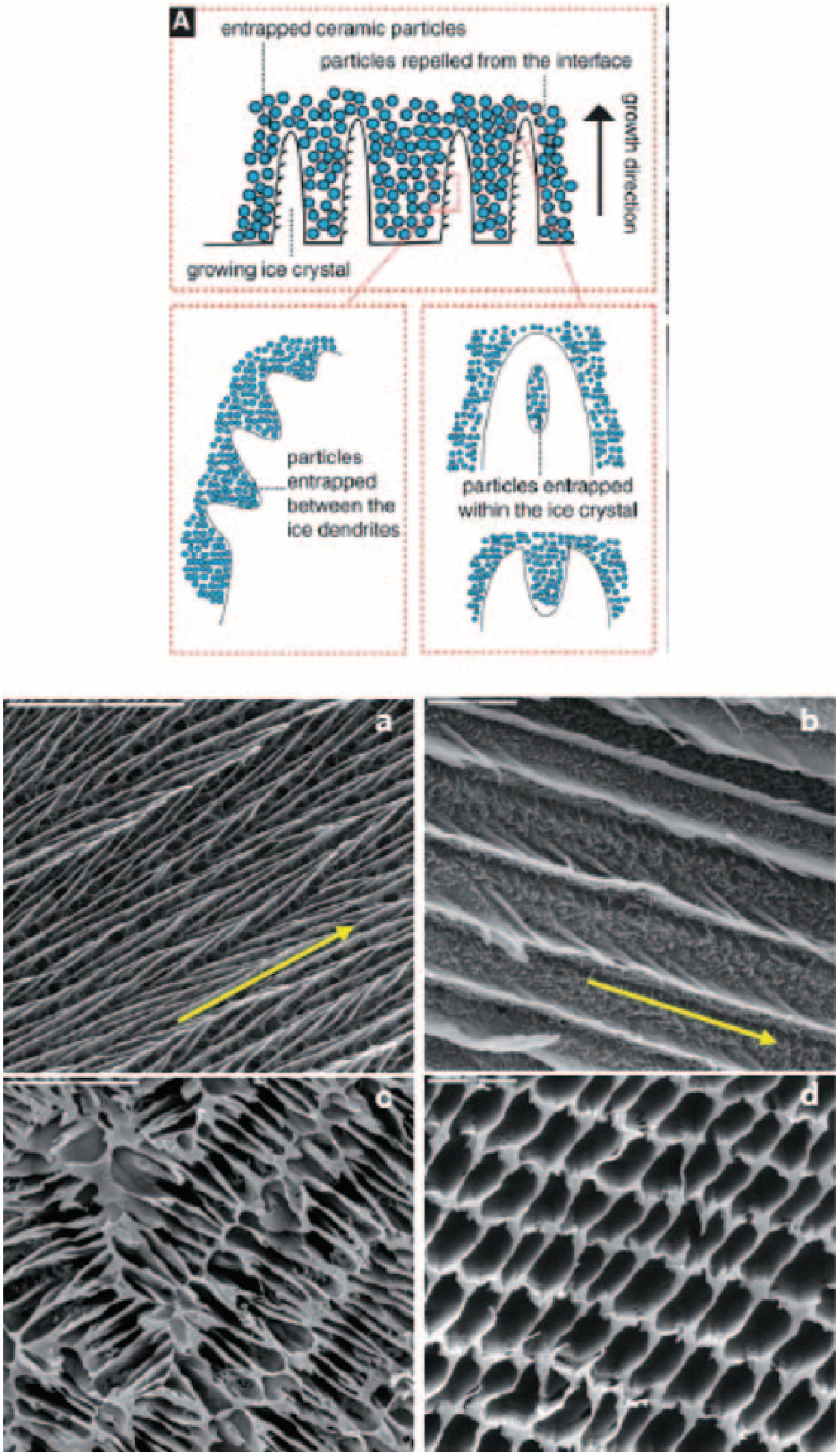


Figure 10. Top: Processing principles and materials. While the sol is freezing, the growing ice crystals expel the ceramic particles, creating a lamellar microstructure oriented in a direction parallel to the movement of the freezing front. Bottom: SEM micrographs of longitudinal (a, b; arrow indicates the direction of freezing) and transversal (c, d) sections of two different PVA hydrogels ISISA bars are 20 μm (reproduced from Ref. 41, with permission).

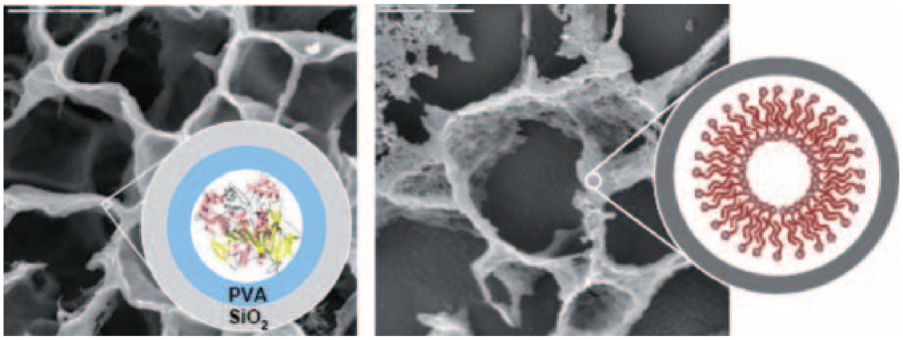


Figure 11. SEM micrographs of the hierarchically organized materials resulting from ISISA processing of a PVA/silica based hybrid hydrogel containing PLE (left) and a binary colloidal hydrogel composed of DMPA liposomes (~100 nm in size) and colloidal silica nanoparticles (1–40 nm in size). Bars are 5 µm (reproduced from Ref. 42, with permission).

after subsequent freeze-drying show a microchannelled structure that corresponds to the empty areas where ice crystals originally resided. Biologicals, such as proteins and liposomes, are easily entrapped within the fences that form the macrostructure.[41]

In the former case, ISISA processing a PVA/silica hybrid hydrogel containing also an esterase protein such as PLE[42] results in an hierarchical bio-hybrid material exhibiting a very sophisticated structure with up to four levels of space organization; that is, the ternary structure of PLE, the PVA (polyvinyl alcohol) domains surrounding esterase, the silica cages entrapping the PVA domains, and the macroporous structure resulting from the cryogenic process.

The PVA nanodomains confer a hybrid nature to the hierarchical material and are crucial for the preservation of enzyme structure and activity (Figure 12).

Furthermore, these hierarchical bio-hybrid materials show an interesting dual character that allows for sharing of tasks (some entities supporting the structure, some other ones providing functionality) and opens the path towards promising applications in the fields of biocatalysis, chromatography, and sensor technology, given the combination of large mass transport with the high internal reactive surface.

This general method starts with the removal of the alcohol released as a by-product during hydrolysis and condensation reactions, based on the gentle vacuum elimination of the alcohol by roto-evaporization, and was first applied to protein entrapment.[43] Similarly, in the encapsulation of bacteria, the roto-evaporization prevents alcohol-mediated membrane lysis (Figure 13) and ensures the formation of open mesoporous structures ideally suited for practical applications.[44] Finally, the presence of gluconamide bulky groups at the cage's surface (coming from the organically modified siloxane precursor GLS) isolates bacteria from silanol groups; enhancing the flexibility of the sol-gel cages.[45] Thus, once again, addressing both the chemical and the structural aspects of the sol-gel material, a general methodology for the entrapment of labile biological actives is achieved which is of relevance for future practical biotechnology applications of silica-based biogels.

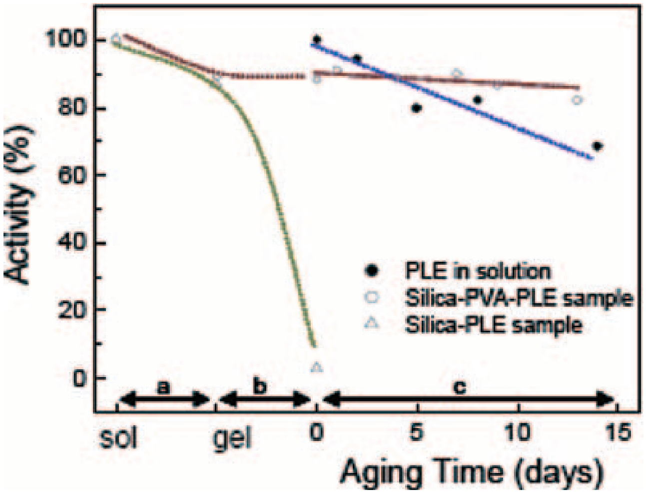


Figure 12. (a, b) Evolution of the enzymatic activity of PLE during formation of the silica (open triangle, green line) and silica-PVA (open circle, red line) samples; (a) gelation and (b) freezedrying. (c) Evolution of the enzymatic activity of PLE in solution (solid circle, blue line) and in the silica-PVA sample (open circle, red line) with aging time (reproduced from Ref. 42, with permission).

7. Conclusions and Perspectives

The numerous and multifaceted results of 20 years of intense research would lead one to think that the area of organic–inorganic hybrid silicas, as a well developed and highly represented field in chemistry, has reached its full potential. Originally used mainly in chromatography, specialized silica gels have evolved into important functional nanomaterials

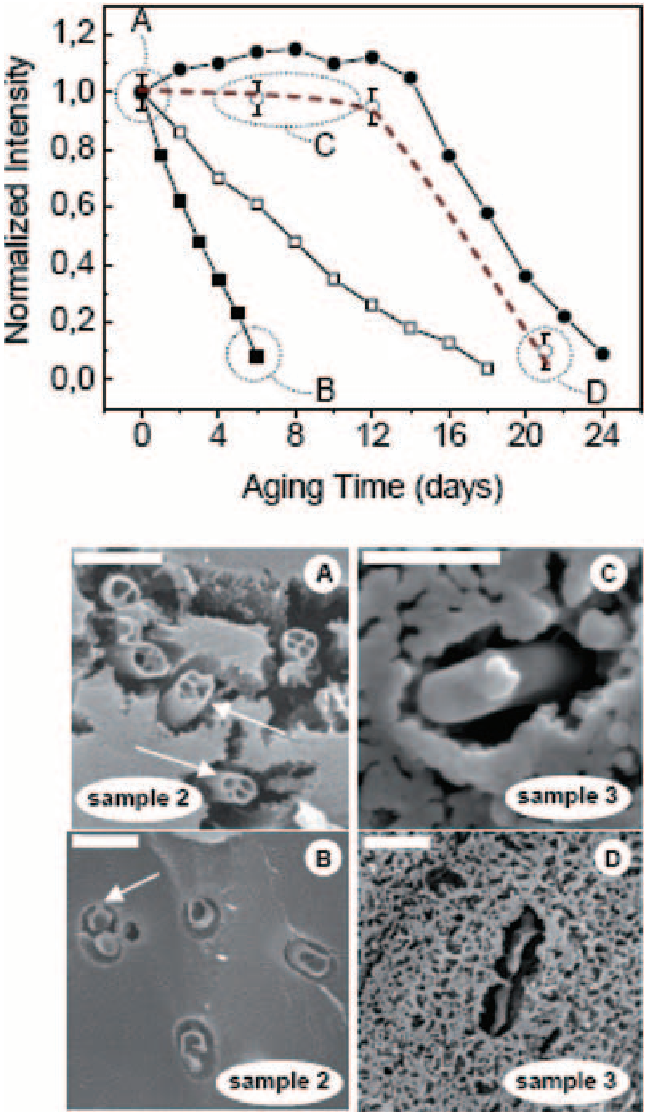


Figure 13. Normalized fluorescence intensity obtained for *E. coli*-GFP encapsulated by the aqueous sol-gel route in hydrogels of different composition: TMOS (tetra-methyl-ortho-silicate) based silica hydrogels (■), GPTMS (3-glycidoxy propyl trimethoxy silane)/TMOS based hybrid silica hydrogels (□), and GLS/TEOS based hybrid silica hydrogels (○). Data for *E. coli*-GFP suspended in a buffered solution are included for comparison (●). Cryo-SEM pictures of *E. coli* encapsulated in TMOS based silica hydrogels (sample 2, A and B) and GLS/TEOS based hybrid silica hydrogels (sample 3, C and D). Bacteria can be visualized as cross-sectioned bacilli because of freeze-fracture (reproduced from Ref. 43, with permission).

suitable for use in electronics, analysis, purification, surface protection, and drug release, while currently, numerous new applications are emerging in a number of fields as diverse as catalysis, medicine, building industry, and biotechnology.[7] For example, sol-gel doped oxides such as ORMOSIL-entrapped lipases discovered by Reetz found practical application shortly after their discovery in the mid 1990s.[46]

In 2006, the \$1 billion global market for sol-gel products (mostly silica-based) was forecasted to increase to \$1.4 billion by 2011 with an average annual growth rate of 6.3% from 2006 to 2011.[47] Actually, this market will increase much faster as many revolutionary products are now reaching the market. In fact, we argue, most relevant applications of silica-based gels are yet to be realized by emulating natural designs which combine hard and soft materials, often in hierarchical architectures, to get synergistic, optimized properties with proven, complex functionalities. This brief account shows how these advancements are starting to take place through tailored, concomitant design of the physicochemical properties along with their morphological aspects both on the macro- and on the nanoscale. Modification of the sol-gel cage hydrophilic-lipophilic balance as well as of its shape and size on the nanoscale (by the employment of surfactants or, even better, through the new ISISA process) during the polycondensation, are likely the two most powerful drivers among the chemical, physical, and structural factors influencing performance. The concepts elucidated in this article will hopefully serve as further guidelines supporting research aimed at the development of new functional silica sol-gels for different applications.

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