The chemical effects of molecular sol–gel entrapment

Mario Pagliaro,[*ab] **Rosaria Ciriminna**[a] **and Giovanni Palmisano**[a]

Received 13th October 2006
First published as an Advance Article on the web 25th January 2007
DOI: 10.1039/b611171h

Chemical conversions within the cages of doped sol–gel porous oxides take place with unique advantages over reactions in solution as the glassy matrix has tremendous effects on the reactivity of the entrapped molecules. The chemical properties of sol–gel materials can be tailored in an immense range of values and chemists are increasingly achieving control on reactions taking place within these matrices, including crucially important photovoltaics. Highlighting recent major advancements, we show in this *tutorial review* how this is actually taking place.

[a] *Istituto per lo Studio dei Materiali Nanostrutturati, Cnr, via U. La Malfa 153, 90146 Palermo, Italy. E-mail: mario.pagliaro@ismn.cnr.it*
[b] *Institute for Scientific Ethics and Methodology, Cnr, via U. La Malfa 153, 90146 Palermo, Italy*

Mario Pagliaro

Mario Pagliaro, is a research chemist and educator based at Palermo's Cnr where he currently works towards the establishment of the International Institute of Scientific Ethics and Methodology (http://www.qualitas1998.net/isem). His research interests focus on the overlap of biology, chemistry and materials science. Since 2004 he has organized the prestigious Seminar "Marcello Carapezza". In 1998 he joined the Cnr where he established a new laboratory now cooperating with researchers of nine countries, financing research by the "Quality College del Cnr" management school.

Rosaria Ciriminna

Rosaria Ciriminna is a research chemist at the Cnr Institute of nanostructured materials based in Palermo. Her scientific interests range from sol–gel materials to photochemistry and natural products. Her work thus far has resulted in the collaborative development of several new catalysts, sensors and chemical conversions. Rosaria has co-authored some 50 research papers on these topics and has been invited to present her work at numerous international conferences.

Introduction

In a visionary 1912 paper entitled *The Photochemistry of the Future*[1] Ciamician predicted that in the future man would have made "batteries based on photochemical processes" and "catalysts to effect solar energy conversion" in electricity and fuel. Yet, one century later, we have only begun to inch toward the future that Ciamician foresaw.[2] Similarly, current chemical synthesis continues to be based on serial reactions and purification steps that require massive amounts of solvents and materials waste, mostly generated in the form of toxic solvents that are eventually incinerated.[3] The average pharmaceutical synthesis, for instance, yields 25–100 kg (including solvent) of waste per kilogram of product which gives the idea of the unsustainable model traditionally adopted by this industry.

The major reasons for such low achievements reside, respectively, in our inability to control the reactivity of (photo)excited molecules and to efficiently segregate reactants from each other. Whereas in Nature efficiency in light use easily exceeds 90%, in man-made processes rapid thermal dissipation of energy occurs and our best molecular photochemical solar cell does not exceed 12% efficiency in full sunlight.[4] On the other side, successful evolution towards sustainable development depends crucially on the availability

Giovanni Palmisano

Giovanni Palmisano, is a PhD student in chemical and materials engineering at the University of Palermo. He currently works at Madrid's Csic Institute of materials with Marisa Ferrer. In mid 2005 he joined Mario Pagliaro's research group. His work focuses on the development of functional materials for electrochemical and photochemical oxidations.

of renewable energy, *i.e.*, electricity from solar light (and hydrogen from water) to replace current dependence (or "addiction to",[5] to quote the current US president) on fossil oil.

In 1996, one of us listened to a presentation in Israel from the inventor of the sol–gel doped materials[6] who called for "bringing chemical reactions from solution to sol–gel matrices".[7] The claim was substantiated by the fact that besides molecular reciprocal segregation, sol–gel molecular encapsulation *i*) dictates accessibility to external reactants through the inner porosity; *ii*) protects and stabilizes the entrapped dopant, and often *iii*) *reduces* restriction compared to common solvents as reaction medium. Hence, for instance, carrying out organic synthesis on sol–gel site-isolated catalysts, the physical separation of reagents or catalysts from each other, traditionally achieved by using separate flasks, enables one-pot conversions in place of consecutive transformation and purification iterations typical of traditional organic synthesis.[3]

We recall here briefly that sol–gel porous oxides are generally obtained by hydrolytic polycondensation of suitable precursors. Taking for example titania doped with a photoactive species (or "sensitizer", eqn (1)) and organosilica-based materials (eqn (2)) this solution chemistry enables to control of the monomer → oligomer → sol → gel → xerogel transition at molecular level.[8]

$$TiCl_4 + H_2O + S \rightarrow S@[TiO_nH_m]_p \qquad (1,\ \text{unbalanced})$$

$$CH_3Si(OCH_3)_3\ +\ Si(OCH_3)_4\ + \\ \text{catalyst} \xrightarrow[H_2O]{MeOH} \text{catalyst}@[(CH_3)SiO_nH_m]_p \qquad (2,\ \text{unbalanced})$$

In general, these oxides show excellent optical quality including high transparency in the visible region that allows fluorescence as well as charge separation processes.[9] Besides catalysis and photovoltaics with entrapped sensitizers incorporated within TiO_2,[10] applications are numerous and range from highly sensitive photochemical sensors[11] to photochromic glasses.[12] The enormous versatility of the sol–gel process in the choice of the process parameters (such as the nature of the precursors, the use of surfactants, acid or base catalysis, and the water/precursor ratio) affords a potentially enormous class of doped materials,[6] either as glassy (amorphous or periodic) or as crystalline solids in which the host–guest interaction can be tailored. After description of the physical bases of the chemistry of ORMOSIL,[13] we focus in this *tutorial review* on the chemical effects of molecular sol–gel encapsulation and show how increasing control on this simple phenomenon is leading to a variety of new chemical processes in sol–gel matrices that are realizing the visions conceived by Ciamician in the 1910s and by Avnir[6] in the 1990s.

The effects of confinement and dispersion

Encapsulation of molecules at the huge inner surface (compared to few $m^2\ g^{-1}$ of external surface) of a sol–gel matrix affords extremely high molecular dispersion in a solid phase. This was clearly established in 1984 in the very first report[14] of molecular sol–gel entrapment describing the photophysical behaviour of Rhodamine 6G confined in SiO_2.

The physical and chemical properties of the entrapped dopants are generally retained. Yet, the efficient isolation of one molecule from the other and the active role played by the sol–gel cage, for instance in dictating accessibility, gives place to a vast new chemistry of sol–gel entrapped molecules which encompasses and goes largely beyond traditional solution chemistry.[6]

In general, confinement of a molecule in solid microporous cages of a solid modifies the electron energy of the molecule, altering in particular the frontier molecular orbital energy.[15] Moreover, entrapped molecules interact with the matrix and its surface by covalent or by noncovalent interactions (van der Waals interaction, π-stacking, electrostatic attractions, and hydrogen bonding) depending on the specific structure of the matrix, of the dopant molecule and on the (chemical or physical) nature of the entrapment.

For example, dyes physically encapsulated in SiO_2 glasses, normally give place to red shift in the positions of the absorption and emission spectra due to interaction of the dye molecules with the internal surface of the porous matrix.

Single molecule caging, originally assumed studying the entrapment of $Ru(bpy)_3^{2+}$ in SiO_2, occurs at low concentrations.[16] Typically, at dopant concentration $>10^{-3}$ M molecular aggregation starts to occur as shown for example by fluorescence studies of silica-entrapped rhodamines (rhodamines tend to form fluorescent aggregates at the adsorbed state, Fig. 1).[17] Hence, whilst at low concentration neither the absorption nor the excitation spectra show signs of aggregation, the excitation spectra of xerogels of increasing SB concentration clearly show (Fig. 2) the formation of fluorescent J-dimers.

On the other hand, high dopant loads (for instance starting from a sol molar ratio composition TEOS : PhTES : dopant = 1 : 1 : 0.4) are useful in photophysical applications where enhanced absorption is sought (TEOS is tetraethoxysilane and PhTES is phenyltriethoxysilane) such as in the case of the UV protective coatings made of transparent phenyl-modified silica films doped with entrapped 2,2-dihydroxy-4-methoxybenzophenone protecting organic materials from light damage.[18]

In the latter case, using an organically modified silica matrix enhances the solubility of the UV absorber in the matrix and allows the preparation of highly loaded coatings. We recall here briefly that in samples prepared without organic substituents, the surfaces of the pores in the resulting matrix consist mainly of uncondensed OH groups, which confer a very polar environment on the pore (57.9 kcal mol^{-1} in the Reichardt $E_T(30)$ scale). Incorporation of R groups into the structure dramatically decreases the cage's polarity with large organic groups hindering further the influence of the residual OH groups at the pores' surfaces. The organic groups are located at the cage's interface, with profound consequences for the homogeneity of the entrapment and the chemical reactivity of the resulting material.[19]

We and others have shown elsewhere[20] that the effects of the hydrophilicity–lipophilicity balance (HLB) of the sol–gel matrix on the chemical *reactivity* of the resulting material are large and mostly due to the enhanced cage flexibility. Referring

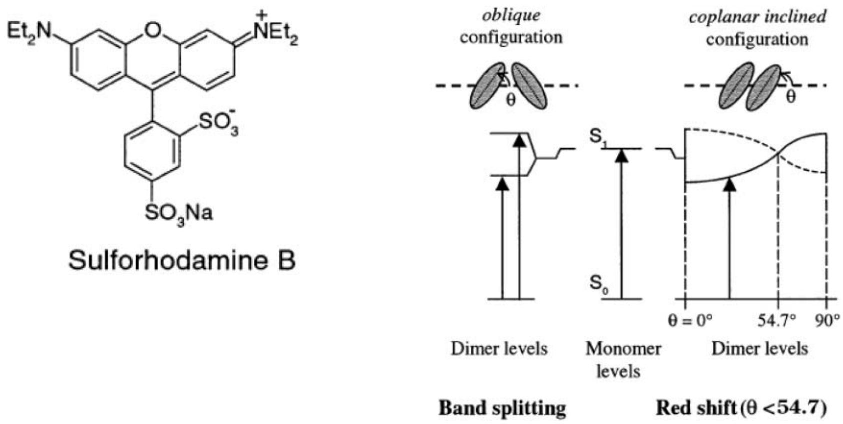


Fig. 1 Molecular structure of SB and exciton band energy diagram for molecular dimers with oblique and coplanar inclined transition dipoles. (Reproduced from ref. 17, with permission. Copyright 2003 American Chemical Society.)

to the the photophysical behaviour of ORMOSIL-entrapped naphthopyrans (Fig. 3) here we emphasize that the shape and the larger size of the *i*Bu groups is also responsible for the increased flexibility of the *i*Bu groups as compared with Me and Ph groups that facilitates the movement of the photochromic molecules inside the pore resulting in faster isomerization kinetics.[21]

Getting back to photochemistry, photochemical reactions are kinetically controlled conversions ubiquitous in Nature where far-from equilibrium phenomena are the rule, rather than the exception. They are generally categorized into two groups:[22] those from equilibrated excited molecules (with reactive species with lifetimes usually in nanoseconds or microseconds); and those from short-lived unequilibrated molecules (with short-lived vibrationally excited species) in which reactivity is relatively insensitive to minor environmental perturbation.

In the early 1960s it became evident that the reaction environment had an important role in dictating the course of photochemical conversions acting on the course of the relaxation processes and stabilizing photoproducts.[23] A constrained medium such as that of a porous matrix or a micelle provides the restricted environment to stop any bimolecular processes that could lead to degradation of the products.

These effects, however, are subtle. For instance, confinement of a molecule within an host instead of leading to inhibition of reactions of the trapped substrate, often results in enhanced reactivity and selectivity because confinement does not mean steric inhibition of *all* motions of the entrapped host molecule which may eventually enjoy less restriction of some motions than in a common solvent.[24] Remarkably analogous findings were established in recent years studying a number of catalytic species entrapped in sol–gel glasses. In particular, molecular entrapment in hybrid organic–inorganic ceramic matrices such as organically modified silicates resulted in enhanced reactivity to transition metal, organo- and enzymatic catalysts, providing clear examples of heterogeneous catalysts in which the solid organic–inorganic surface participates actively in the reaction mechanism.[24] Interestingly, Nature uses similar confinement of photoactive molecules within

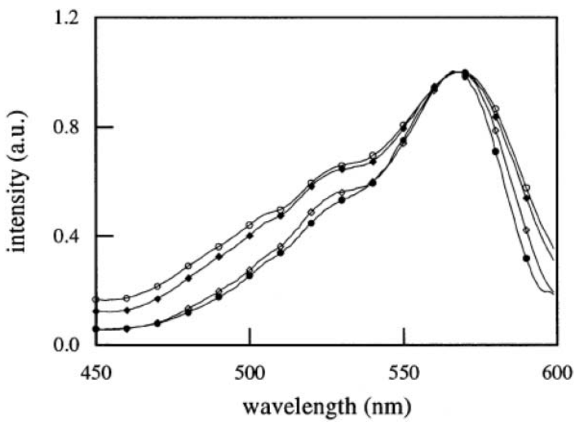


Fig. 2 Excitation spectra (λ_{em} = 650 nm) of SB-doped xerogels of increasing (●→○) SB concentration. (Reproduced from ref. 17, with permission. Copyright 2003 American Chemical Society.)

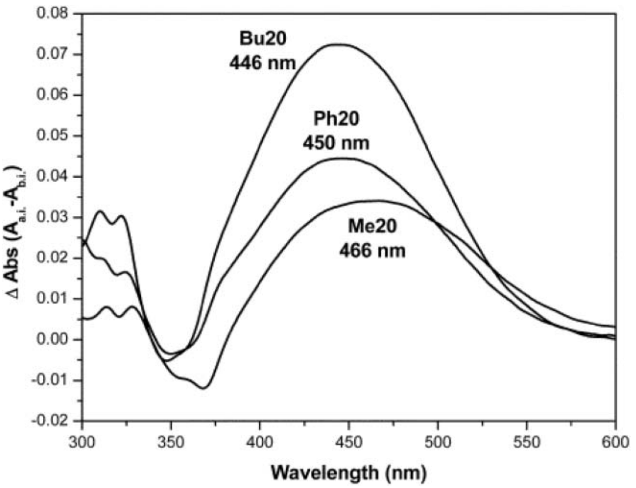


Fig. 3 UV-Vis spectra of ORMOSIL-embedded naphthopyran with different modifying groups show that samples prepared with *i*Bu and Ph groups lead to more significant shifts to the UV compared with samples prepared with the same relative amount of Me groups. (Reproduced from ref. 21, with permission. Copyright 2005 Royal Society of Chemistry.)

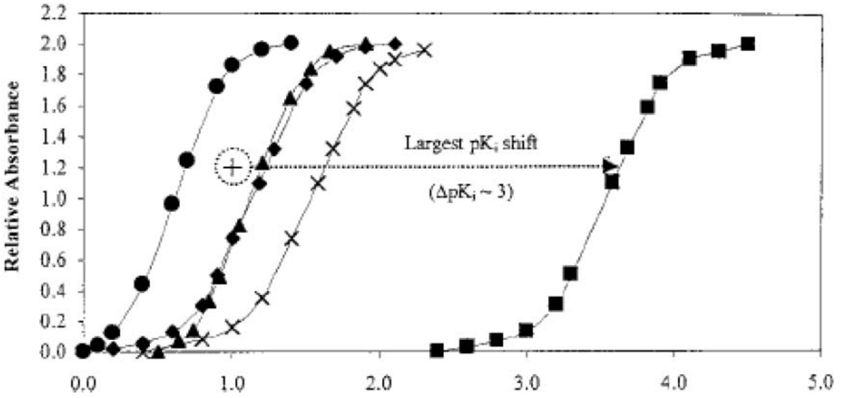


Fig. 4 Photochemical titration curves of the crystal violet co-entrapped in silica sol–gel matrices with different surfactants, no-surfactant (◆) and value in solution (×) shows the impressive variations in the sensing properties for the same entrapped dye. (Reproduced from ref. 28, with permission. Copyright 2001 American Chemical Society.)

proteins and it exploits the resulting weak guest–host interactions to achieve the immense proficiency typical of chemical processes taking place in the biological realm. A variation of 20 Å in the distance between donors and acceptors in protein, for instance, changes the electron-transfer rate by 10^{12}-fold.[25] Therefore, by a fine selection of this distance only (proteins are effectively entrapped in sol–gel glasses), one may expect to change the rate of biological electron transfer by similar order of magnitudes.

Similarly, enzymes achieve high activity and selectivity by precise organization of chemical functionality in the inner and outer spheres surrounding the active site;[26] and a new successful approach to heterogeneous catalysis is based on just tailoring the cooperative properties of hybrid organic–inorganic interfaces in sol–gel materials.[27]

Micelle/molecule co-entrapment: Tuning dopant's chemical reactivity

While the sol–gel matrix can usefully preserve the properties of the dopant, the reverse is also true in that changing the sol–gel cage environment may well influence the properties of the dopant itself. This has been demonstrated by careful co-entrapment in a single sol–gel interphase of different surfactants along with a dopant dye (crystal violet, Fig. 4) as fluorescent pH sensor observing changes in the sensing properties of the resulting materials from large magnitudes to delicate fine-tuning.[28] In other words, different reactivities for the *same* molecule can be accessed by tailoring the heterogeneous microenvironment of the molecule, thus creating a library of reactivities from a *single* specific compound.

In place of applying synthetic methods to alter a chromophore reactivity, this new way of control chemical reactivity involves choosing an appropriate solid micellar system (from the available multitude) and exploiting it in manipulating the chemistry of the entrapped compound. The sol–gel matrix and the micellar solubilization, in fact, have a synergetic effect: Their combination produces effects stronger and more tuneable than in solution, so that a careful selection of sol–gel entrapped surfactants allows enormous changes in the dopant properties to be induced.

Site-isolation and charge separation

Sol–gel encapsulation opens the route to new applications that become possible since entrapped excited molecules cannot diffuse (giving place to the thermal energy dissipation typical of molecules in solution). This, as shown below, has important consequences for both photochemistry and catalysis.

Photochemistry. Upon entrapment, enhancements in the charge separation rate in the order of 10^2–10^6 times faster than the charge recombination process are common, affording 10-fold increase in the lifetime of excited species in the sol–gel matrix compared to lifetime in solution, such as in the case of photoinduced electron transfer in SiO_2-co-entrapped pyrene and methylviologen.[29] Furthermore, sol–gel entrapped molecules are physically and chemically protected. For example, room temperature phosphorescence under regular atmospheric conditions is observed from SiO_2-entrapped dyes which in solution is observed only at cryogenic temperatures and in vacuum.[30] Similarly, organic fluorophores encapsulated in ORMOSIL nanoparticles (Fig. 6) become 20 times brighter (comparable to that of quantum dots, and one to two orders of magnitude brighter than free dye, Fig. 5) and more photostable than their constituent fluorophore due to protection of the entrapped dye exerted by the cage against bleaching by oxygen.[31]

Photoinduced charge separation analogous to that reported above is of paramount importance, for instance in the case of

Fig. 5 Fluorescent core–shell silica nanoparticles incorporating organic dyes with different spectral characteristics, covering the entire UV-vis absorption and emission wavelengths. (Reproduced from ref. 31, with permission. Copyright 2005 American Chemical Society.)

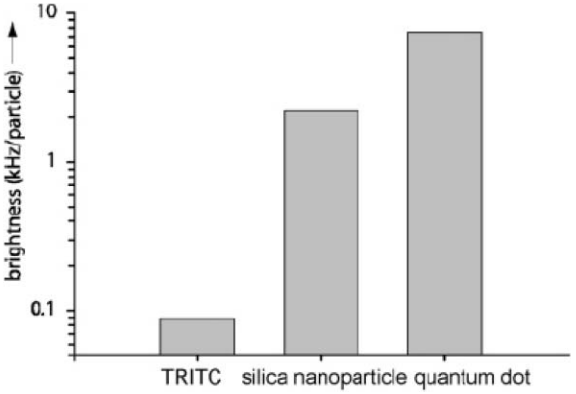
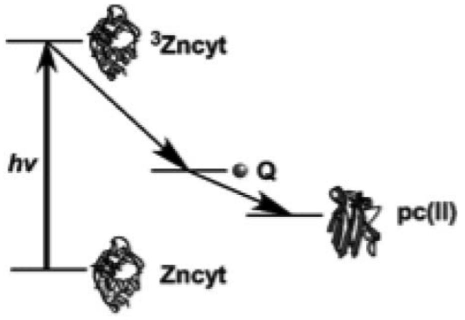


Fig. 6 Brightness comparison for dye TRITC, silica nanoparticles and quantum dots. The brightness values are obtained from FCS measurements of the count rate per particle at intensities below which fluorescence saturation and photobleaching occur. (Reproduced from ref. 31, with permission. Copyright 2005 American Chemical Society.)

sol–gel entrapped proteins. Proteins present a uniform electronic barrier to electron tunnelling and a uniform nuclear characteristic frequency, properties similar to an organic glass. Accordingly, encapsulating metalloproteins in sol–gel silica glass mimics sequential electron transfer for which ultimately the energy of *visible light* is converted to reducing equivalents for plastocyanin and cytochrome c (Scheme 1).[32]

The immobilized electron acceptor is either cupriplastocyanin, pc(II), or ferricytochrome c, cyt(III); and the mobile charge carrier is the redox couple $\text{FeEDTA}^{-/2-}$ or $\text{Ru(NH}_3)_6{}^{3+/2}$. The redox processes are photoinduced: Zncyt (zinc-substituted cytochrome, the immobilized electron donor) is excited by the laser pulse and converted to the triplet state, ^{3}Zncyt (a strong reducing agent).

Whereas encapsulation in sol–gel glass does not affect proteins' intrinsic redox properties, the rigid silica glass spatially separates the proteins from each other. The small inorganic complexes, $\text{FeEDTA}^{-/2-}$ and $\text{Ru(NH}_3)_6{}^{3+/2+}$, move through the glass pores, react with the encapsulated metalloproteins, and establish the interprotein electron transfer. In the glassy matrix, the electron-transfer reactions between ^{3}Zncyt and pc(II) and between ^{3}Zncyt and cyt(III)—rapidly taking place in solution—are *completely suppressed* in the absence of a charge carrier.



Scheme 1 Encapsulating metalloproteins in sol–gel silica glass enables conversion of the energy of *visible light* to reducing equivalents for plastocyanin and cytochrome c. (Reproduced from ref. 32, with permission. Copyright 2002 American Chemical Society.)

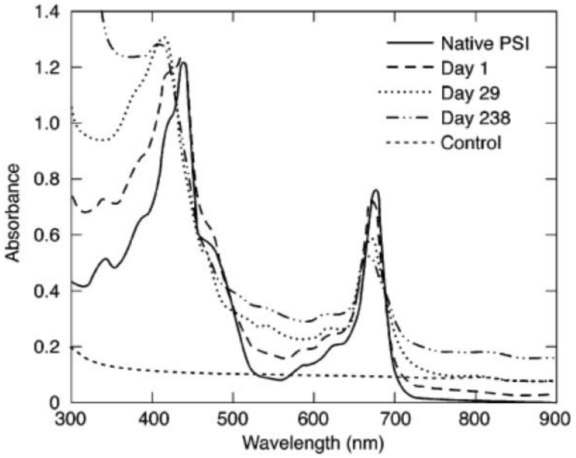
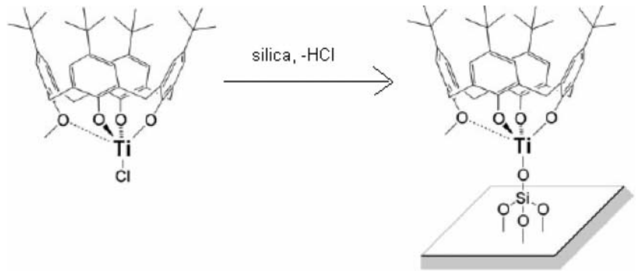


Fig. 7 Visible absorption spectra of Photosystem I entrapped in sol–gel at intervals during the aging process compared with the solution spectrum of the native preparation. The spectrum of a control gel without PSI that was aged for 29 days is also shown. (Reproduced from ref. 33, with permission. Copyright 2005 American Chemical Society.)

Similarly, sol–gel immobilization and stabilization of photosystem I in a SiO_2 glass (PSI, one of the naturally occurring molecular photovoltaic structures part of the photosynthetic apparatus of higher plants and algae) affords a photoactive material capable to undergo photochemical oxidation and photoinduced hydrogen production (Fig. 7).[33] This indicates that both the intramolecular electron-transfer apparatus of the P700 reaction centers and the intermolecular electron-transfer function retain full functionality upon entrapment of such a large transmembrane protein complex.

The magnitude of the photochemical response of the immobilized sample after 29 days (when the majority of the water had been removed) is slightly greater than the native sample. Shrinkage of the porous silica framework with time (sol–gels are "living" materials)[8] reduces the conformational freedom of the entrapped enzyme molecules. Hence, as the gel-ageing process progressed to 238 days, the response became vanishingly low.

Catalysis. Sol–gel entrapment affords catalysts of superior, and often unique, performance in a number of conversions under widely different reaction conditions.[24] Accordingly, many such catalytic materials mostly based on doped silica xerogels are commercially available.[34] The planarity and macroscopic rigidity of a sol–gel surface, for example, can be used for stabilizing coordinatively unsaturated species that are catalytically inactive in solution such as in the case of simultaneous coordination of a multidendate ligand and of SiO_2 surface to the Ti–calixarene complex in Scheme 2.[35] While the precursor molecule in Scheme 2 has limited activity and selectivity for epoxidation of unfunctionalized olefins in solution, the site-isolated heterogenized catalyst is comparable to the fastest Ti epoxidation catalysts. Indeed, entrapment stabilizes the metal complex against dimerization; while all the catalytic centers are entrapped at the surface of a vast porosity, where they are accessible even to bulky reactants.



Scheme 2 Grafting of the inactive complex calixarene–TiCl on SiO_2 (left) results in single-site alkene epoxidation catalyst of pronounced selective activity. (Reproduced from ref. 35, with permission. Copyright 2004 American Chemical Society.)

We now consider physically entrapped catalysts. Once entrapped in an organosilica matrix, the oxidation catalyst NPr_4RuO_4 does not leach in solution and smoothly mediates the aerobic conversion of a variety of structurally different alcohol substrates with a 5-fold activity enhancement over homogeneous reaction. Encapsulation also ensures stable activity of the material by preventing association of the reduced Ru species that in solution gradually results in the formation of an inactive black sol precipitate. The entrapped molecules are mutually isolated and cannot enter autocatalytic cycles. Thus, whereas TPAP in solution rapidly decomposes hydrogen peroxide to water and O_2, TPAP@SiO_2 smoothly mediates the oxidation of alcohols to carbonyls with H_2O_2 as atom-efficient oxidant provided that peroxide is added slowly (Fig. 8).[36]

In the case of sol–gel catalysts, leaching and loss of activity typical of polymer-supported catalysts and other heterogenization approaches[37] is prevented by the use of ligands covalently anchored onto silica. For example, a variety of different hydroformylation reactions can be carried out over silica-entrapped rhodium bound to Xantphos ligands under batch[38a] or continuous flow[37,38b] conditions with the catalyst showing constant activity over a period of more than a year.

Such large protectability of the sol–gel cage has tremendous consequences for biochemical applications using entrapped enzymes. For example, by entrapment in (surfactant modified) silica sol–gel matrixes, alkaline phosphatase keeps functioning under extremely acidic environments, and acid phosphatase works smoothly under extremely alkaline environments.[39] This is due to the unique fact that large pH changes in very small local environments—such as the free space between the outer surface of the protein and the silica surface of the cage—actually mean very small variations in the number of caged protons (Fig. 9).

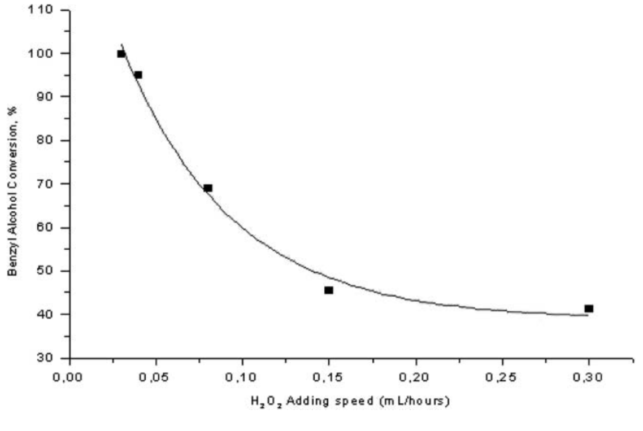


Fig. 8 Benzyl alcohol conversion as function of the velocity of H_2O_2 addition in the presence of silica-entrapped TPAP. (Reproduced from ref. 36, with permission. Copyright 2004 Elsevier.)

Supposing that the water layer is a small reservoir of 100 water molecules, and that the external pH is 0, then the hydronium ions penetrate that reservoir until equilibrium is reached and a nominal ‘‘pH 0’’ is obtained also in said layer's volume. From the point of view of the protein, this means that the protein gets protonated by only two protons (‘‘pH 0’’ means 2 moles H_3O^+ for each 100 moles water) which are enough to compensate for the extreme pH gradient while clearly pose no stress at all for the encapsulated protein.

Similar protectability of entrapped enzymes coupled to the versatile chemistry of ORMOSIL can be utilized advantageously such as in the case of entrapped alkaline proteases, which are commonly used in liquid detergents and washing powders to help remove proteins and other stains from dirty clothes.[40] The doped ceramic beads synthesised from the precursor bis[3-(trimethoxysilyl)propyl]ethylenediamine (enTMOS) swell upon addition of water and release the enzyme right when they are needed, therefore ensuring both protection of the valued enzymes during product storage and full functionality during usage.

The versatility of the sol–gel process enables other unique catalytic applications. For example, organic reactions is water. Beyond a general methodology for carrying out catalytic conversions in H_2O mediated by doped ORMOSIL in the presence of a modest amount of surfactant,[41] another recent method for the waste-free oxidation of alcohol affords high yields of commercially valued carbonyl compounds in water with complete selectivity and remarkable stability.[42]

The method uses a simple electrode made of a thin film of sol–gel organosilica doped with nitroxyl radicals deposited on the surface of an indium–tin-oxide (ITO) electrode. Thus, whereas in water benzyl alcohol is rapidly oxidised to benzoic acid, the use of the hydrophobic sol–gel molecular electrode TEMPO@DE affords benzaldehyde only (Scheme 3), with an unprecedented purity, which is highly desirable for the fragrance and pharmaceutical industries where this aromatic aldehyde is employed in large amount.

Finally, another general catalytic methodology made possible by sol–gel materials is based on the concept of supported ionic liquid catalysis in supercritical phase (*sc-Silc*). The method combines the advantages of ionic liquids as solvent booster; dense phase carbon dioxide as reaction (and extraction) solvent; and immobilized metal catalyst for easy product separation and catalyst recycle.[43] A mesostructured silica gel co-incapsulating the ionic liquid imidazolium and the aerobic metal catalyst selectively mediates the oxidative dehydrogenation of numerous alcohols in dense phase CO_2. No traditional organic solvent is used to extract the product out of the ionic liquid and at the end of the reaction the CO_2 is

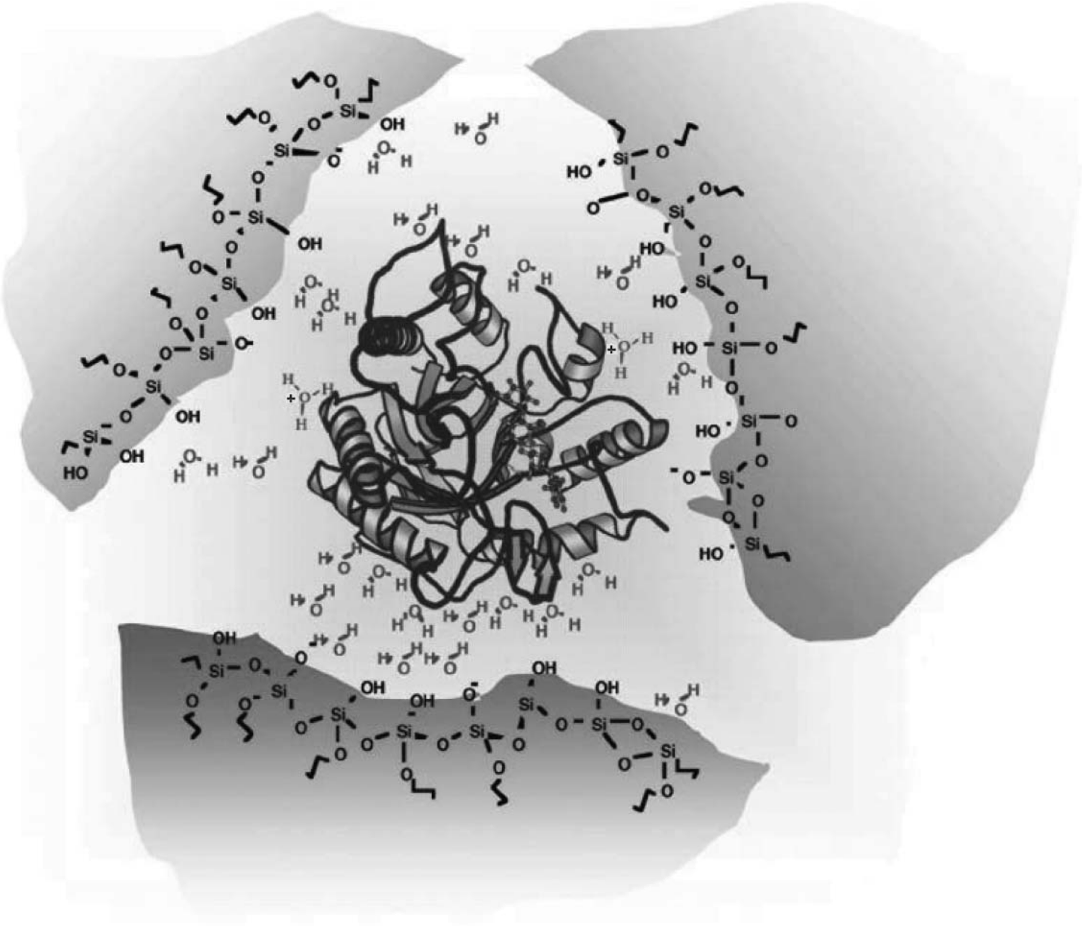
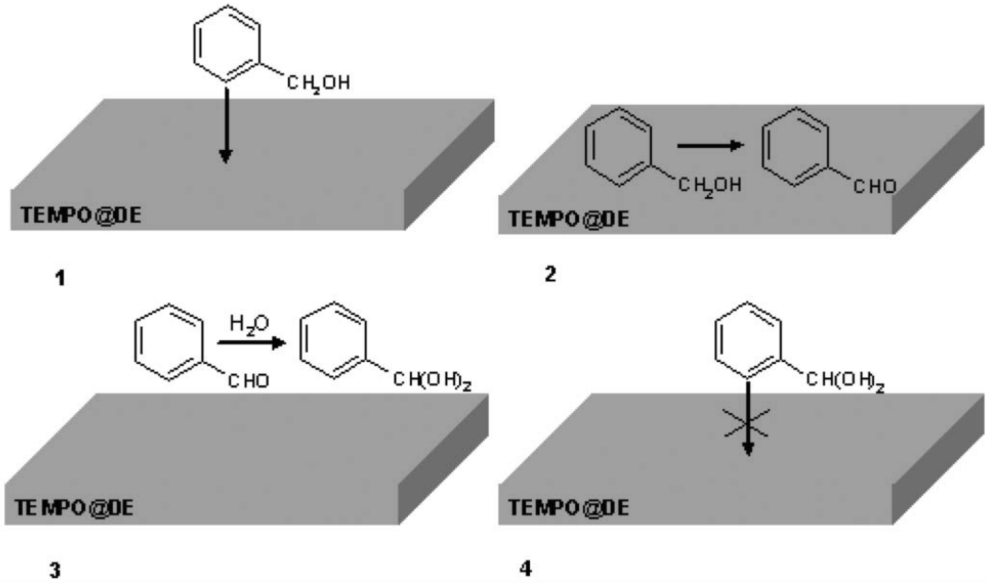


Fig. 9 Schematic view of the entrapped enzyme with a few water molecules inside a cage, two of which are protonated. The nominal ''pH'' is very low. (Reproduced from ref. 39, with permission. Copyright 2005 American Chemical Society.)



Scheme 3 Alcohols are oxidised at the inner surface of TEMPO@DE (**1** → **2**). But not so the hydrated aldehydes (**3** → **4**) which cannot enter the pores due to the hydrophobicity of the material's surface. (Reproduced from ref. 42, with permission. Copyright 2006 WILEY-VCH.)

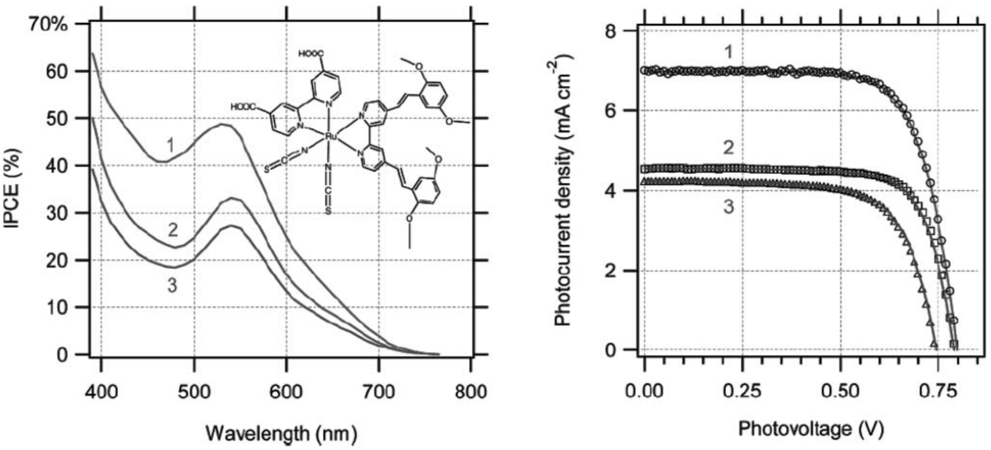


Fig. 10 Efficiency (left) and photocurrent–voltage characteristics (right) of a solar cell based on TiO_2 films sensitized by N945 (inset shows its chemical formula). Pluronic-templated three-layer film (1); non-organized anatase treated by $TiCl_4$ (2); non-organized anatase non-treated by $TiCl_4$ (3). (Reproduced from ref. 44, with permission. Copyright 2005 American Chemical Society.)

easily vented off by simple pressure release leaving the solid catalyst unmodified and ready for reuse.

Photovoltaics

Achieving efficient photovoltaic processes—conversion of the *hν* photons energy into electric energy—implies achieving effective charge separation between the excited sensitizer S* and the free electron, formed upon transfer of an electron to the interface of the solid matrix.[10] If the interfacial charge-separated pair has a sufficiently long lifetime, it may undergo subsequent bimolecular redox processes forming useful chemical fuels, such as H_2 and O_2.

Here, sol–gel encapsulation of Ru-based dyes having a broad range of visible light absorption at the surface of porous TiO_2 nanocrystalline film has resulted in molecular solar cells that are good candidates to replace costly photovoltaic panels based on ultrapure crystalline silicon.[4]

Complete visible light absorption is due both to efficient electron transfer from the excited chromophore into the conduction band of TiO_2 (which requires a high electronic coupling between the dye and the semiconductor for efficient charge injection), and to the long ($>$10 μm) path length of the porous film. In this case, material's structural organization improves performance (Fig. 10) and organized mesoporous TiO_2 films exhibit solar conversion efficiency about 50% higher compared with films of the same thickness made from randomly oriented anatase crystals.[44]

This improvement results from a remarkable enhancement of the short circuit photocurrent which in its turn is due to 5-fold enhanced roughness of a 1 μm-thick film and thus to an accessible huge surface area. A similar solar cell (Tandem Cell, with an efficiency of 7.5%) is about to be commercialized for the production of hydrogen through water splitting (Fig. 11).

A layer of TiO_2 nanoparticles less than 30 nm thick is used for collecting photons and converting them into electrons, directly splitting water into its constituent elements using two solar cells that together can capture sunlight from all parts of the UV spectrum to provide hydrogen at significantly lower cost than alternative processes.[45]

Conclusion and perspectives

The Earth's population of 6 billion is growing in number and wealth and will need ever more energy and raw materials. Thus, our common development will depend on the economic availability of renewable energy as well as of new synthetic methods in place of wasteful traditional chemical processes. Nature employs photosynthesis and catalysis to obtain the cornucopia of substances and structures benefiting life with impressive efficiency and with practically no waste. Enabling real merging of materials science with biochemistry, doped sol–gel materials are opening the route to uniquely advanced catalytic and photosynthetic processes. Thus, we argue, photochemistry and catalysis within sol–gel oxides will play a crucial role in our evolution towards sustainable development.

Sol–gel oxides doped with catalytic and photoactive molecules offer unprecedented performance in a number of applications and are disclosing new avenues to practical employment of heterogeneous catalysis and photochemical reactions. As leading photochemists recently put it, "organic

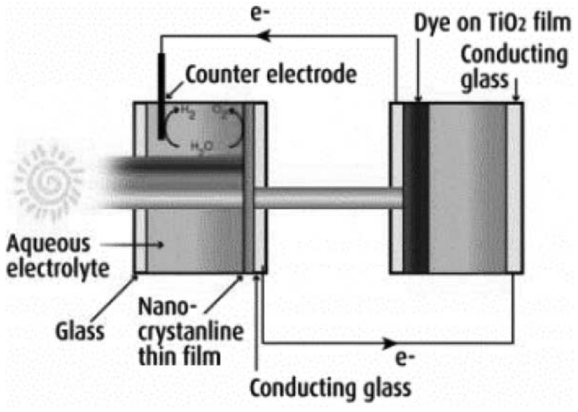


Fig. 11 Photo-catalysis by nano-crystalline thin films in the Tandem Cell produces hydrogen directly from sunlight and water approaching 7.5% efficiency: Renewable energy with no carbon dioxide emissions. (Reproduced from ref. 45, with permission. Copyright 2006 Hydrogen Solar Ltd.)

glass medium provides closer host–guest interactions than those in many organized media. And tapping such a medium effect could be a new way of controlling photochemistry”.[23]

Tuning the interfacial physico-chemical properties of the host matrix ultimately allows control of the reactivity of the entrapped guest molecules which, counter to intuition, often enjoy enhanced freedom compared to their solution state in common solvents. Similarly, in catalysis the hybrid organic–inorganic surface acts synergistically with other organic moieties (*i.e.*, ligands) to stabilize specific catalytic or chromophore assemblies (or a given transition state) that are often absent in homogeneous solution due to competition with translational entropy.[27]

Chemists are eventually learning to design and synthesize similar functional doped materials with dramatic enhancement in the material’s activity and selectivity compared to solution chemistry. New research will rely more frequently on computational chemistry tools in guiding experimental work, as recently shown for dye-doped TiO_2[46] or for silica-entrapped vanadium.[47] Moreover, co-entrapment of surfactant and active molecules aimed to induce changes similar to those observed with a pH sensor will likely find widespread use. In the end, this will speed transfer of sol–gel catalytic and photochemical technologies from the laboratory to industry and eventually to numerous applications in daily life. The development of functional sol–gel materials is certainly one of the most exciting fields of modern chemical research.

Acknowledgements

M.P dedicates this article with affection to Professor Gianfranco Nuzzo (Palermo) whose teachings of classics in the 1980s are a constant source of inspiration. Our work owes much to the teachings, and example, of David Avnir (Jerusalem) and Arjan de Nooy (today in Den Haag). Thanks to Sandro Campestrini (Padova), Laura Ilharco and Alex Fidalgo (Lisboa), Joël Moreau, Peter Hesemann and Michel Wong Chi Man (Montpellier), Frank Bright (Buffalo), Michele Rossi (Milano), Eric Le Bourhis (Poitiers), Daniel Mandler (Jerusalem), D. Tyler McQuade (Ithaca), Carsten Bolm (Aachen), Marisa Ferrer (Madrid), Jose Sepulveda Arques (Valencia) for fruitful collaboration. Financial support from the Quality College del Cnr is gratefully acknowledged.

References

1 G. Ciamician, *Science*, 1912, **36**, 385.
2 D. Nocera, *Chem. Eng. News*, 2001, **79**(13).
3 S. J. Broadwater, S. L. Roth, K. E. Price, M. Kobaslija and D. T. McQuade, *Org. Biomol. Chem.*, 2005, **3**, 2899.
4 P. Wang, S. M. Zakeeruddin, J. E. Moser, M. K. Nazeeruddin, T. Sekiguchi and M. A. Gratzel, *Nat. Mater.*, 2003, **6**, 402.
5 G. W. Bush, *State of the Union Address* (January 31, 2006). Available at the URL: http://www.whitehouse.gov/stateoftheunion.
6 D. Avnir, *Acc. Chem. Res.*, 1995, **28**, 328.
7 Professor David Avnir, at the The Hebrew University of Jerusalem, November 1996.
8 L. M. Ilharco and A. Fidalgo, *Chem.-Eur. J.*, 2004, **10**, 392.
9 C. Sanchez, B. Lebeau, F. Chaput and J.-P. Boilot, *Adv. Mater.*, 2003, **15**, 1969.
10 J. M. Stipkala, F. N. Castellano, T. A. Heimer, C. A. Kelly, K. J. T. Livi and G. J. Meyer, *Chem. Mater.*, 1997, **9**, 2341.
11 R. M. Bukowski, R. Ciriminna, M. Pagliaro and F. V. Bright, *Anal. Chem.*, 2005, **77**, 2670.
12 M. Zayat and D. Levy, *J. Mater. Chem.*, 2005, **15**, 3769.
13 M. Pagliaro, R. Ciriminna, M. Wong Chi Man and S. Campestrini, *J. Phys. Chem. B*, 2006, **110**, 1976.
14 D. Avnir, D. Levy and R. Reisfeld, *J. Phys. Chem.*, 1984, **88**, 5956.
15 A. Corma, H. García, G. Sastre and P. M. Viruela, *J. Phys. Chem. B*, 1997, **101**, 4575.
16 D. Avnir, V. R. Kaufman and R. Reisfeld, *J. Non-Cryst. Solids*, 1985, **74**, 395.
17 M. L. Ferrer and F. del Monte, *Langmuir*, 2003, **19**, 650.
18 P. Garcia Parejo, M. Zayat and D. Levy, *J. Mater. Chem.*, 2006, **16**, 2165.
19 For a thorough discussion on these and related structural aspects, see ref. 13.
20 A. Fidalgo, R. Ciriminna, L. M. Ilharco and M. Pagliaro, *Chem. Mater.*, 2005, **17**, 6686.
21 R. Pardo, M. Zayat and D. Levy, *J. Mater. Chem.*, 2005, **15**, 703.
22 R. S. H. Liu and G. S. Hammond, *Photochem. Photobiol. Sci.*, 2003, **2**, 835.
23 R. S. H. Liu and G. S. Hammond, *Acc. Chem. Res.*, 2005, **38**, 396.
24 R. Ciriminna, L. M. Ilharco, A. Fidalgo, S. Campestrini and M. Pagliaro, *Soft Matter*, 2005, **1**, 231.
25 C. C. Moser, J. M. Keske, K. Warncke, R. S. Farid and P. L. Dutton, *Nature*, 1992, **355**, 796.
26 X. Zhang and K. N. Houk, *Acc. Chem. Res.*, 2005, **38**, 379.
27 J. M. Notestein and A. Katz, *Chem.-Eur. J.*, 2006, **12**, 3954.
28 C. Rottmann and D. Avnir, *J. Am. Chem. Soc.*, 2001, **123**, 5730.
29 A. Slama-Schwok, M. Ottolenghi and D. Avnir, *Nature*, 1992, **355**, 240.
30 D. Levy and D. Avnir, *J. Photochem. Photobiol. A*, 1991, **57**, 41.
31 H. Ow, D. R. Larson, M. Srivastava, B. A. Baird, W. W. Webb and U. Wiesner, *Nano Lett.*, 2005, **5**, 113.
32 E. V. Pletneva, M. M. Crnogorac and N. M. Kostic, *J. Am. Chem. Soc.*, 2002, **124**, 14342.
33 H. O’Neill and E. Greenbaum, *Chem. Mater.*, 2005, **17**, 2654.
34 Including the versatile oxidation catalyst Silia CatTEMPO™ recently commercialized by Canada-based SiliCycle. For an overview of commercial sol–gel catalysts, see: R. Ciriminna and M. Pagliaro, *Org. Process Res. Dev.*, 2006, **10**, 320.
35 J. M. Notestein, E. Iglesia and A. Katz, *J. Am. Chem. Soc.*, 2004, **126**, 16478.
36 S. Campestrini, M. Carraro, U. Tonellato, M. Pagliaro and R. Ciriminna, *Tetrahedron Lett.*, 2004, **45**, 7283.
37 For an interesting discussion of catalyst separation and recycling, see: D. J. Cole-Hamilton, *Science*, 2003, **299**, 1702.
38 (*a*) A. J. Sandee, J. N. H. Reek, P. C. J. Kamer and P. van Leeuwen, *J. Am. Chem. Soc.*, 2001, **123**, 8468; (*b*) A. J. Sandee, R. S. Ubale, M. Makkee, J. N. H. Reek, P. C. J. Kamer, J. A. Moulijn and P. W. N. M. van Leeuwen, *Adv. Synth. Catal.*, 2001, **343**, 201.
39 H. Frenkel-Mullerad and D. Avnir, *J. Am. Chem. Soc.*, 2005, **127**, 8077.
40 B. C. Dave, K. Deshpande, M. S. Gebert and J. C. McAuliffe, *Adv. Mater.*, 2006, **18**, 2009.
41 R. Abu-Reziq, D. Avnir and J. Blum, *Chem.-Eur. J.*, 2004, **10**, 958.
42 G. Palmisano, R. Ciriminna and M. Pagliaro, *Adv. Synth. Catal.*, 2006, **348**, 2033.
43 R. Ciriminna, P. Hesemann, J. Moreau, M. Carraro, S. Campestrini and M. Pagliaro, *Chem.-Eur. J.*, 2006, **12**, 5220.
44 M. Zukalova, A. Zukal, L. Kavan, M. K. Nazeeruddin, P. Liska and M. Grätzel, *Nano Lett.*, 2005, **9**, 1789.
45 The cell was recently developed by the UK-based company Hydrogen Solar together with Altair Nanotechnologies in Nevada (US). For more information: http://www.hydrogensolar.com.
46 M. Nazeeruddin, F. De Angelis, S. Fantacci, A. Selloni, G. Viscardi, P. Liska, S. Ito, B. Takeru and M. Grätzel, *J. Am. Chem. Soc.*, 2005, **127**, 16835.
47 M. Tada, N. Kojima, Y. Izumi, T. Taniike and Y. Iwasawa, *J. Phys. Chem. B*, 2005, **109**, 9905.