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Sol-gel microencapsulation of odorants and flavors: opening the route to sustainable fragrances and aromas

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The sol-gel approach to encapsulate fragrance and aroma chemicals in porous silica-based materials has the potential to afford odorant and flavoured materials with novel and unique beneficial properties. Amorphous sol-gel SiO₂ is non-toxic and safe, whereas the sol-gel entrapment of delicate chemicals in its inner pores results in pronounced chemical and physical stabilization of the entrapped actives, thereby broadening the practical utilization of chemically unstable essential oils. Reviewing progress in the fabrication of diverse odorant and flavoured sol-gels, we show how different synthetic strategies afford advanced materials suitable for practical application with important health and environmental benefits.

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Key learning points

- The encapsulation of fragrances and flavors in sol-gel porous silicas solves many of the problems encountered with traditional polymeric systems.
- Intrinsic advantages include chemical and physical stabilization of the entrapped actives, inertness of the encapsulating glass matrix, transparency, and a high mechanical resistance.
- The technology is versatile enabling the preparation of simple xerogel matrix particles, through sophisticated core-shell microcapsules and composite capsular systems.
- Encapsulated natural fragrances can now be conveniently used with numerous health and environmental benefits, replacing with encapsulated essential oils the toxic synthetic perfumes widely employed in personal care products and perfumes.
- Microencapsulation in silica-based microspheres makes it possible the formulation of perfumes in water and alteration of the perfume original notes.

Introduction

Microencapsulation of flavors and fragrances is a topic of relevant interest in either academy or industry as shown, for example, by the numerous scientific symposia devoted to the subject.¹ Fragrance chemicals are added to an ample variety of consumer products including perfumes, laundry detergents, fabric softeners, soaps, detergents, and personal care products; whereas aroma chemicals are widely employed by the food industry to enhance taste. Accordingly, the flavor and fragrance industry is an important sector of the chemical industry (sales in 2011 estimated at 21.8 billion \$);² and traditionally an important contributor to research in organic chemistry.³ Today this industry uses an extensive range of encapsulation technologies, as microencapsulated flavors and fragrances of improved efficacy are demanded for a wide range of applications including cosmetics (perfumes), personal care (hand and

body wash, toothpaste, etc.), food (flavors) and home care (laundry and detergents).⁴

In cosmetics, household and personal care products, a common objective is to extend the life and improve the delivery of the highly volatile fragrances allowing the gradual liberation of the encapsulated functional species, namely controlled release of the active ingredients. There is also great interest in infusing scent into everyday materials such as fabrics;⁵ or in turning liquid flavors into free-flowing powders so as to increase their shelf life in food products.⁶

Significant health and environmental benefits, too, may originate from the efficient encapsulation of fragrances. For example, most of the synthetic nitro- and polycyclic musks used in perfumes, deodorants and detergents are toxic and non-biodegradable. As a result, they tend to accumulate in the environment⁷ and in human mother's milk.⁸ Natural fragrances that thus far could not be used due to poor chemical and physical stability might replace non-biodegradable musks as a consequence of the chemical and physical stabilization of the labile fragrance molecules in the sol-gel silica matrix.

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Amongst the new encapsulation technologies introduced in the last decade,⁴ the sol-gel encapsulation of scented and aromatic organics in nanostructured porous silicas is a promising alternative to encapsulation in organic polymers.⁹ Compared to polymers, for example, sol-gel glasses do not swell or change structure under pH or temperature variations. Further advantages include relative inertness or a low degree of chemical interaction of the matrix material with the encapsulated active, transparency, thermal protection of the active, protection against oxidation and a high mechanical resistance. Finally, amorphous silica obtained by the sol-gel process is non-toxic and biocompatible (in the US it has the GRAS status and is approved as a flavor carrier with up to 2% in weight in the final food), is resistant to microbial attack; and can be used to encapsulate both water-based and oil-based liquids.

Finally, the sol-gel entrapment methodology allows us to effectively control the way the active entrapped compounds are released, which for industry is at least as important as efficient compartmentalization.¹⁰

The only review on sol-gel SiO_2 nanosols doped with liquid organics was published by Böttcher and co-workers in 2005.¹¹ The first literature reports on sol-gel encapsulation of fragrances and aromas in matrix silica particles, in turn, date back to the late 1980s. Research has continued, mainly in industry, with recent research reports describing the encapsulation of flavors and fragrances in sophisticated silica microcapsules (see below). Reviewing the story of this evolution, and aiming to identify new opportunities for progress, this account summarizes the basic knowledge emerging from almost three decades of research. This account is concluded with an outlook offering arguments supporting our opinion that sol-gel derived fragrant and flavoured products will soon reach the marketplace.

Sol-gel encapsulation in matrix particles

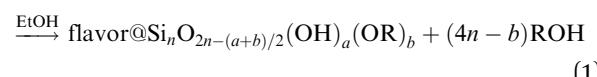
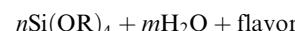
Organic molecules are effectively entrapped within the inner pores of silica-based xerogel matrix particles either by simple



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addition of the dopant molecules before the hydrolysis of Si alkoxide precursors, in the presence of a mutual solvent such as ethanol,¹² or starting from completely hydrolyzed $(\text{SiO}_2)_n$ nanosol precursors by adding the organic species directly to the aqueous nanosol, since encapsulation actually occurs in the condensation step,¹³ with the further advantage that now the ratio of the organic to the inorganic composite can be altered by simple mixing, while the composition of the sol can be adapted to take into account the solubility of the organic liquid species.



Organically modified silicates (ORMOSILS), too, can be easily obtained by the same approach using organically-modified silicon alkoxides as co-precursors.¹⁴

Eqn (1) describes the overall process affording a molecularly doped amorphous silica gel. In general, tetraethylorthosilicate (TEOS) and related ethyl-modified alkoxides are the precursors of choice in cosmetic, medical and food applications of sol-gel derived silicates, since aqueous ethanol byproducts of the process are generally tolerated.

The sol-gel process has been studied in detail, for example by vibrational spectroscopy.¹⁵ The hydrolysis and condensation reactions take place at localized regions; whereas silica polymerizes in stages to nuclei of silica eventually leading to the formation of sol particles that incorporate the flavor molecules into the sol.

Actually, the reaction above never results in the formation of the pure oxide, as the residual valence electrons on siloxane ($\text{Si}-\text{O}-\text{Si}$) have the ability to react with water resulting in a surface covered with silanol groups ($\text{Si}-\text{OH}$), rendering highly polar the final silica matrix.¹⁶ As put by Avnir, the inventor of doped sol-gel glasses,¹² it is precisely the fact that $a \neq 0$ in eqn (1), and thus that a large number of unreacted silanol



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groups exist at the material's surface thereby creating a large inner porosity, which gives place to the impressive variety of chemical applications of doped sol-gel silicas.

In comparison to microencapsulation within traditional coating polymers, the sol-gel encapsulation within the silica cage results in significant chemical and physical stabilization of the entrapped dopant. Such chemical and physical stabilization due to molecular entrapment in the sol-gel cage has been shown since the very first paper describing, in 1984, a silica-entrapped dye (rhodamin 6G).¹⁷

The first report on the sol-gel entrapment of fragrances in silica xerogel particles dates back to 1987 when a Japanese research company was granted a patent entitled "Perfume compositions produced by sol-gel methods".¹⁸ Patents on flavor adsorption on amorphous silica, on the other hand, date back to 1968,¹⁹ and today silica gels are widely employed by the food industry as flavor carriers to turn liquids into free-flowing powders of enhanced shelf life.²⁰

Studying one such material, namely limonene adsorbed on amorphous silica, Reineccius in 1992 reported the enhanced oxidative stability of the flavor supported on SiO_2 compared to limonene supported over organic food carriers.²¹ Fragrances and flavors, indeed, are usually made of compounds having two or more conjugated double bonds which are easily oxidized by oxygen, with consequent alteration of the perfume's odour note or of the flavor's taste.

In 1997, Carturan and co-workers entrapped perfumed essences (geranial, β -ionone and menthol) in ORMSIL matrices, and studied the release kinetics.²² The work was finalized to prepare materials with graded, slow release of actives, and the team synthesized a series of ORMSIL xerogels obtained from 1:1 TEOS-MTES precursor mixtures (MTES = methyl-triethoxysilane) polycondensed under acidic conditions ($\text{pH} = 1.5$).

The team found that ethanol was released during the process, and the essences entrapped as volatile organic species ($S = \text{ethanol} + \text{essence}$) were released as a function of time according to exponential curves. The release kinetics were mainly attributed to differences in matrix porosity and chemical interactions of the organic molecules with the matrix, a relevant outcome that apparently was not further explored in subsequent years.

In 1999, Böttcher and co-workers published the general method to encapsulate organic liquids in SiO_2 xerogels and thin film coatings starting from completely hydrolyzed (SiO_2)_n sols, as mentioned above.¹³ The team reported exponential decay release curves from silica-entrapped liquid fragrances. Furthermore, the release of a complex mixture of fragrant molecules from both bulk xerogels (Fig. 1) and coating systems (Fig. 2) was found to occur in a two-step process.

The fast initial liberation process caused by the low activated evaporation of the substances from open pores at the surface of the bulk material is followed by a much slower process from the internal porosity, pointing to the strong activated diffusion of the remaining liquid from inside the sol-gel cages.

Soon afterwards, the same researchers based in Germany investigated the use of doped silica coatings to functionalize textiles,²³ with mixtures of entrapped common essential oils

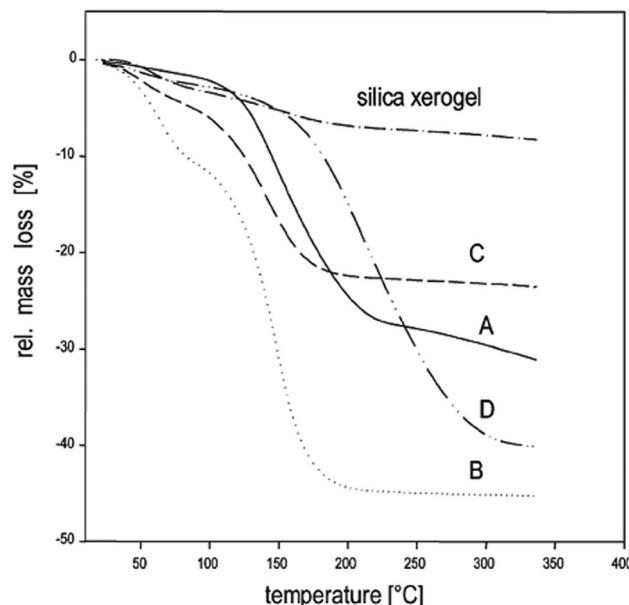


Fig. 1 Thermogravimetric analysis of silica xerogels with embedded liquids (A = nitrobenzene; B = formamide; C = citronella; D = dimethylphthalate). [Reproduced from ref. 12, with kind permission.]

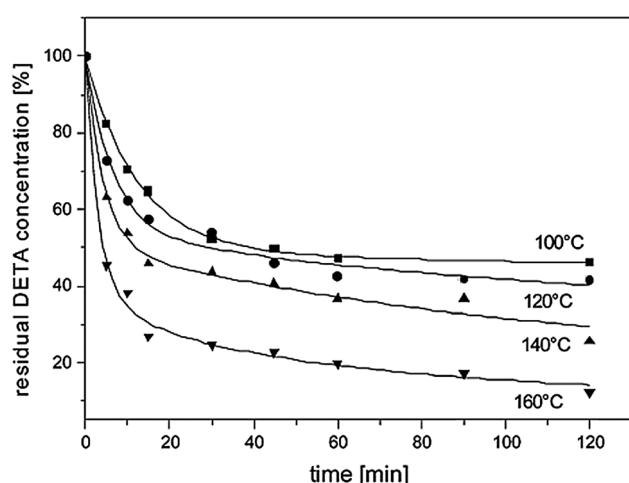


Fig. 2 Release of DETA (diethyltoluamide) from silica coatings on polyester foil at different temperatures. [Reproduced from ref. 12, with kind permission.]

(lavender, eucalyptus, thyme, balm, rosemary, sage, peppermint, basil, marjoram and ginger); as well as with entrapped eucalyptol, camphor and menthol for the therapeutic treatment of the diseased respiratory tract.

Efforts were aimed to prepare prolonged fragrant articles, such as flavor-releasing garments with well-being or healing effects. Essential oils indeed are well known for their various wellness indications such as refreshing, calming, and relaxing effects and relief of congestion.²⁴

Their sol-gel encapsulation within silica coatings afforded fragrant fleece retaining odour, over a period of 85 days during which the same exponential decay of the flavor concentrations was observed. However, the two-step course of release of Fig. 1

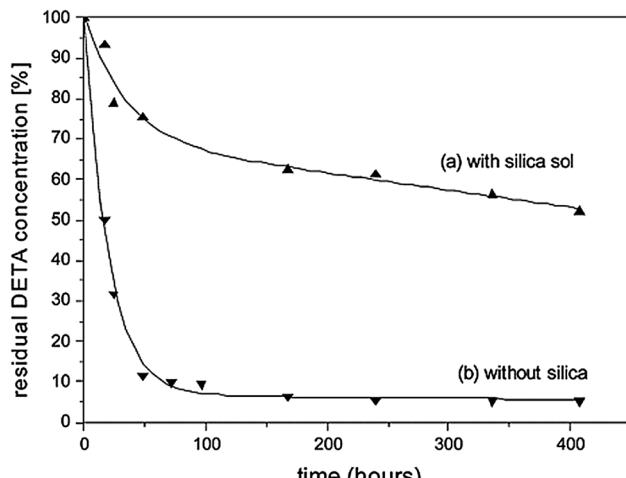


Fig. 3 Evaporation of DETA from cellulose fleece in an air stream: (a) coated with the composite sol E; (b) without silica sol. [Reproduced from ref. 12, with kind permission.]

was now found to be blurred because the natural flavors contain a mixture of different volatile components. An outcome that, incidentally, shows that upon sol-gel immobilization the release profile of a perfume is changed; and therefore the original scent of the neat perfume (normally consisting of three different liquids with very different optimized volatility) is changed.

The team, however, proved that immobilisation and controlled release of aromatic liquids within a modified silica coating was feasible, offering new opportunities for functionalising textiles.

For example, a cellulose fleece treated with a silica coating embedding insect repellent DETA (*N,N*-diethyl-*m*-toluamide) and citronella almost entirely retains the active ingredient, whereas the same fabric impregnated with pure DETA or citronella liquids rapidly lose most of the ingredients (Fig. 3).

Interaction of odorant molecules with the silica sol-gel cage

The sol-gel entrapment of different odorant molecules (alcohols, esters, aldehydes and terpenes) in SiO_2 matrix particles made by sol-gel processing of TEOS was studied by Pratsinis and co-workers from Nestlé, a large food company in the early 2000s.²⁵

In detail, the retention performance decreases in the order alcohols > aldehydes \geq esters > terpenes, due to the different chemical interactions between the dopant and the surface Si-OH groups. Nonpolar compounds like terpenes, on the other hand, are poorly retained due to lack of chemical interaction with the silica surface.

Molecules that do not interact, or interact only physically with the SiO_2 surface are released first, followed by chemically adsorbed ones. Hence, alcohols, that hydrogen bond to the Si-OH groups through oxygen free π -electrons, are best retained, followed by aldehydes that, too, are well retained due to their ability to form hemiacetals. Particles with an open porosity show increased retention with increased loads, whereas denser

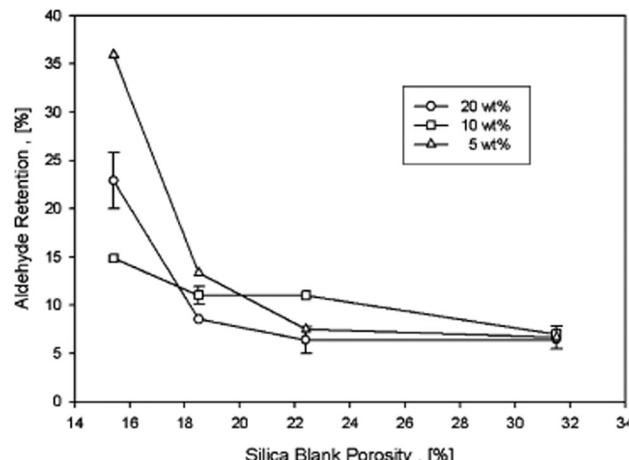


Fig. 4 Average aldehyde retention (hexanal, octanal, and decanal) in SiO_2 xerogels as a function of porosity for total initial aroma loadings of 5, 10, and 20 wt%. [Reproduced from ref. 25, with kind permission.]

matrices reveal a reduced retention with increasing load. Especially for lower initial loads, the retention was significantly increased with decreasing porosity.

For example, for an initial alcohol load of 5 wt%, the retention was enhanced by about 5-fold by halving the porosity, pointing to enhanced nanoconfinement in the cage space. Following the same trend, the average aldehyde retention of a mixture of aldehydes (hexanal, octanal, and decanal) entrapped in silicas at initial loadings of 5, 10, and 20 wt% increases with decreasing porosity (Fig. 4). In other words, in contrast to carbohydrate matrices, where increased aroma load leads to decreased retention, for sol-gel silica matrices the fragrance load and release kinetics are coupled.

In practice, the initial load, affecting the size of the sol-gel cages where the dopant molecules are entrapped, affects the release kinetics. As a result, higher loadings induce larger pore structures from which the aroma is lost much faster compared to smaller cages at low loadings. The authors therefore concluded that both aspects (encapsulation performance and release kinetics) need to be taken into account when designing an artificial flavor mixture for sol-gel encapsulation.

Pratsinis and Veith also studied encapsulation and release of decanoic acid (a model flavor) in TEOS-derived xerogel particles obtained using the two-step sol-gel process (acid-hydrolysis followed by base-condensation) and by varying the hydrolysis ratio $H = [\text{H}_2\text{O}]/[\text{TEOS}]$ from 5.1 (sample A, in Fig. 5) through 37.3 (sample F).²⁶

Powders with larger porosity E and F show the lowest retention, whereas retention in densest sample A is twice as high, showing that nanoconfinement in the silica sol-gel cages is considerably more effective in denser gel structure obtained from a slowly hydrolyzing silica nanosol, in which the more porous silica particles are able to deform during drying and effectively entraps the flavor molecule.

Again, a result of this study was that the dopant molecules act as templates of the sol-gel cages. Indeed, in comparison to the corresponding blank samples, the increase of porosity upon

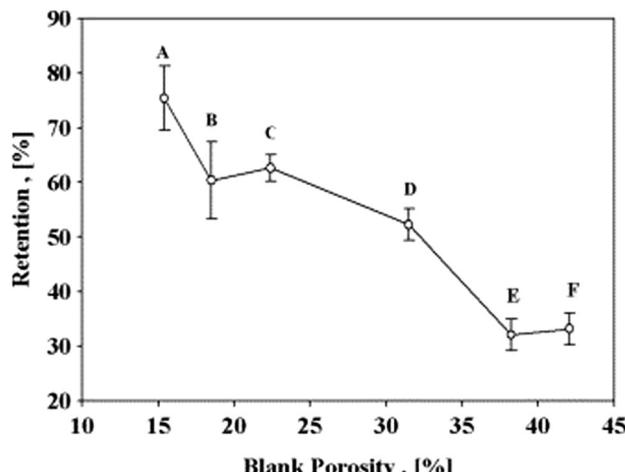


Fig. 5 Decanoic acid retention (GC analysis) in various silica powders as a function of porosity of the corresponding blank powders. Flavor retention increases with decreasing porosity indicating that a denser matrix prevents diffusional losses. [Reproduced from ref. 26, with kind permission.]

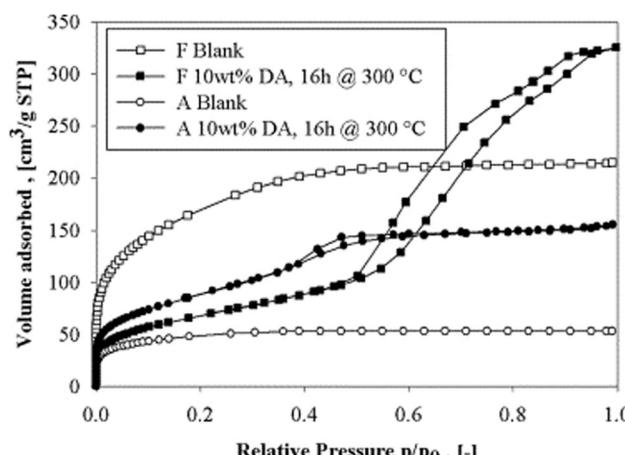


Fig. 6 Adsorption isotherms of blank (open symbols) sol-gel powders A and F and of the corresponding ones loaded with 10 wt% decanoic acid (DA) (filled symbols) after DA removal by heating for 16 h at 300 °C. In contrast to the blank adsorption isotherms, the DA-laden powders exhibit a Type IV isotherm after DA removal. [Reproduced from ref. 26, with kind permission.]

entrapment of dodecanoic acid in densest sample A was significantly greater than in sample F (Fig. 6), with porosity going from 15.4% in the blank sample to 37.4% for sample A, and from 42.1% in the blank sample to 52.8% in sample F.

Finally, heat treatment of the flavor-loaded powders up to 200 °C for a prolonged time showed the well known chemical and physical stabilization of the sol-gel entrapment,¹⁴ as no physical or chemical deterioration of the entrapped acid was observed, contrary to the most frequently employed materials for flavor adsorption, such as gum Acacia and starch.

From sol-gel matrix particles to capsules

The entrapment of liquid organic substances in spherical microcapsules either from oil-in-water (O/W) or from water-in-oil

(W/O) microemulsions was independently described by Avnir²⁷ and Barbé²⁸ in the early 2000s. Instead than in water and co-solvent alcohols only, the sol-gel polycondensation is now carried out in a microemulsion (Scheme 1), and takes place within the emulsified droplets affording spherical microcapsules of core-shell geometry in which a thin shell of silica or organosilica encapsulates the functional species.

The method allows effective isolation and protection of valued dopant molecules.²⁹ Fig. 7, for example, shows a striking microtomography image of liquid limonene encapsulated in a silica sphere, as obtained by researchers at Australia's Ceramisphere.

The same team led by Barbé recently showed how trans-retinol (Vitamin A), a valued cosmetic anti-aging ingredient very sensitive to oxidation, once encapsulated in organosilica 0.3 μm micro-particles (12–14% w/w) results in retinol retaining activity for a much longer time, compared with similar commercial stabilized retinol products.³⁰

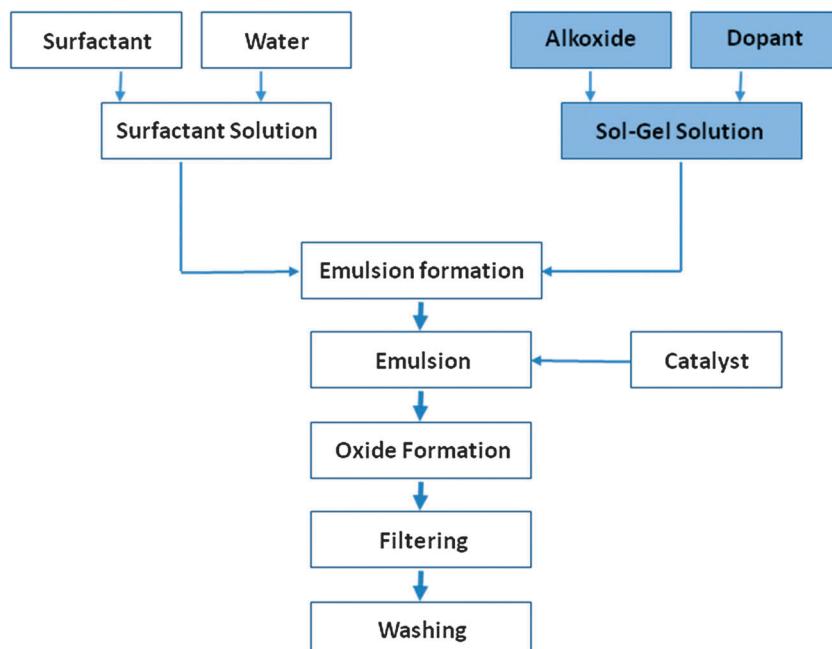
In general, the micron-sized capsules of core-shell geometry contain very high loads of active ingredient (up to 90% in weight of the final materials) and usually release the ingredient through mechanical rupture or dissolution of the shell, with release usually being slower and of longer duration, due both to reduced surface area and pore volume in the microsphere and to differences in surface morphology of the particles produced by emulsification or casting and grinding (ground granules have an irregular shape, angular geometry and multiple cracks, while the sol-gel microspheres are smooth spheres whose surfaces are formed in contact with the emulsifying bath).³¹

Alternative release paths to control release in different microenvironments become possible, as exemplified by the release mechanism of benzoyl peroxide encapsulated silica microcapsules used in commercial therapeutic formulations for treating acne, where the skin's sebo penetrates the capsules and extracts the active compound.³²

The technology is particularly well suited for the micro-encapsulation of fragrance mixtures. For example, along with Ilharco and coworkers we recently investigated the entrapment of bergamot oil in different silica-based microcapsules obtained from O/W microemulsions.³³ The most efficient entrapment of this essential oil, today a widely employed top note in perfumery,³⁴ occurs in silica microcapsules from ammonia-catalyzed condensation of TEOS, affording microspheres with a uniform silica coating free of surface imperfections. All chemicals, including the most abundant and volatile terpenes comprising the valued essential oil, are effectively encapsulated in the core of the SiO₂ capsules with no chemical alteration.

Being smooth, visually attractive and easily formulated in water or in oil the resulting spherical silica microcapsules are well suited for cosmetic applications, for example in personal care and in cleaning product compositions such as body wash, liquid soap, skin cream and shampoos.

Accordingly, several recent patent applications describe the benefits of entrapping fragrances, perfumes, aromas and flavors as core in a shell of SiO₂, made via emulsification of fragrance oils containing TEOS.



Scheme 1 Preparation of doped core/shell particles via the sol-gel process. Key is the combination of: emulsion-polymerization and sol-gel chemistry. The RT production of glass now takes place in the emulsion droplets acting as micro-reactors, affording microencapsulated actives of all sort. [Reproduced from ref. 29, with kind permission.]



Fig. 7 X-ray micro-tomography image of a Ceramisphere (a trade mark of Ceramisphere Pty Ltd) containing encapsulated limonene clearly seen as liquid bubbles. [Photo courtesy of Dr Sherry Mayo, CSIRO, reproduced with kind permission from ceramisphere.com.]

Data in Table 1 from one patent application³⁵ filed by IFF, a large flavor and fragrance company, illustrate how once applied through an anti-perspirent (AP) roll-on base silica capsules doped with a fragrance retain their odor much better

Table 1 Panelist evaluation of fragrance in SiO_2 microcapsules [Reproduced from ref. 33, with kind permission.]

Sample	Fragrance intensity immediately after application, I_0	Fragrance intensity 5 h after application with rubbing, I_{5h}	I_{5h}/I_0
Neat fragrance	16.5	9.8	59
SiO_2 capsules	14.5	13.5	93

The product containing the capsule (100 μl) in AP roll-on based was applied to the forearm of six panelists and the fragrance intensity was evaluated by 20 intensity judges immediately after application and 5 h after application upon rubbing the applied product.

than neat fragrance. Rated from a scale ranging from 0 to 30 the numerical values of fragrance intensity suggest whether the fabric only produces very weak intensity (value of 5) or generates a strong smell (a value of 30). After rubbing the doped capsule the intensity was almost unvaried, whereas the intensity of the product containing the neat fragrance was almost halved.

Further progress towards sol-gel capsules with enhanced mechanical properties was recently described by Givaudan, another large flavor and fragrance company.³⁶ Now, the oily active ingredient is first entrapped in a traditional gelatin core-shell capsule made by coacervation with a gelatin/gum arabic capable of forming a hydrogel shell around the active ingredient. This polymer-caged core is thus mixed with TEOS to form a composite shell of silica particles interspersed between the polymeric lattice.

The resulting composite hydrogel/capsules possess shells with a high Young's modulus, meaning that even though they are easily broken under small applied deformation, mechanically they are far more resistant under small loads as compared to traditional coacervate capsules. In contrast to SiO_2 capsules that need to be compressed by more than half their original size to burst, the capsules with a polymer–silica composite shell allow the release the active ingredient at a small much smaller deformation of the capsule; which is advantageous for example in food applications.

The researchers carried out again sensory evaluation tests, for example with encapsulated peppermint oil in a toothpaste or encapsulated fragrance applied in a skin cream. In each case, the panels judged the encapsulated products to be superior to the non encapsulated counterparts.

Outlook and perspectives

The sol-gel process to make silica-based materials doped with flavor and fragrance species is a convenient alternative to traditional microencapsulation methods that, taking place at room temperature, prevents the degradation of the delicate included compounds. The methodology, first used in 1987, has evolved from encapsulates made of irregular SiO_2 xerogel particles, to sophisticated core-shell particles capable of encapsulating high amounts of functional organic species, and effectively releasing the entrapped species. Yet, to the best of our knowledge, no commercial products exist that make use of silica-encapsulated odorant or aromatic species, despite the numerous advantages summarised in this account.

For example, while silica gels are extensively used as flavor carriers, despite intense research activities on silicas doped with fragrant molecules, including the production of industrial prototypes, up to now no sol-gel encapsulated flavor or fragrance products have been commercialized. Asked to comment on this situation, an industry's practitioner³⁷ emphasized that, while his company has not yet commercialized perfumed sol-gel based products, it manufactures and markets Si-elastomers (*i.e.* silicones) as perfume matrices for use in toilets, cars, big stores, where slow and prolonged release of the microencapsulated fragrances successfully takes place.

Only in perfumery and in personal care, at least three major obstacles can be solved by encapsulation in safe silica-based particles, ranging from: (i) formulation of sol-gel entrapped perfumes of tuneable scent,³⁸ through (ii) alcohol-free perfumes formulated in water avoiding skin irritation,³⁸ to (iii) stabilized natural fragrances replacing toxic synthetic musks. One might therefore ask the reasons for this lack of innovative odorant and flavoured products based on the sol-gel technology and if this situation will likely change or not.

We believe that new sol-gel delivery systems will soon be introduced by cosmetic and flavor and fragrance companies for two basic reasons. The first is that the innovation can now be made clearly visible to consumers. In the case of toxic sunscreens, for example, the side effects of organics absorbed by the skin were eliminated. Hence, Merck aptly uses the term "sunglasses for the skin" to market ethylhexyl methoxycinnamate and related organic UV filters sol-gel entrapped in (not visible) 1.0 μm transparent SiO_2 capsules formulated in water, to a large variety of cosmetic companies.³⁹

The second reason supporting our argument is that, following the emergence of these and related new sol-gel silica products, the price of both TEOS as well as of aqueous silica colloids has dropped significantly.⁴⁰ In the late 1990s, the price of TEOS was so high that the start-up biotechnology company (IRB) established in Italy by Carturan and co-workers to encapsulate living cells opted to build its own plant to manufacture TEOS starting from SiCl_4 and ethanol.

In the early 2000s, Germany's Merck asked Sol-Gel Technologies, then a start-up specializing in sol-gel materials, to conduct the scale up of their technology to manufacture sol-gel entrapped sunscreens. When the technology was proven successful, the larger company internalized the process, bought the manufacturing unit in Israel and expanded production at another site in Germany to supply an ever increasing customer base.

A similar route can be envisaged for microencapsulated fragrances and aroma species.

Companies specializing in performance materials will use different proprietary sol-gel routes to manufacture functionalized silica-based materials, based on customer (cosmetic, perfume, household and personal care, laundry and food companies, among many others) requirements.

Beyond the technical and economic feasibility of sol-gel derived fragrances and flavors, which now appears obvious, the positive consequences for human health and the environment should not be underestimated. Ubiquitous toxic synthetic fragrances are posing serious threats that must be faced. Recent research has shown that synthetic perfumes are highly mutagenic at *femtomolar* concentrations, and cause significant neuromodulations in human neuroblastoma cells at extremely low levels of concentration.⁴¹ Essential oils, in contrast, are renewable natural products showing multiple beneficial health effects. Yet, they are chemically unstable in the presence of air, light, moisture and high temperature, justifying somehow industry's reliance on poorly biodegradable synthetic perfumes, even though their poor sustainability profile is now well known; similarly, the skin irritating and sensitization power of absolute ethanol used to dissolve oily perfumes, making fragrances formulated in water a desirable, and yet distant, objective of chemical research in perfumery is well known.⁴²

Getting back to the first main argument that advantages can now be made clearly visible to the customer, the sol-gel encapsulation in SiO_2 and in silica-based materials of environmentally benign but unstable fragrances and aromas offers unprecedented long-term stability, which is of course a crucial requirement for any economically viable product. It is somehow revealing therefore to notice how recent research in the field targets exactly the stabilization of essential oils in an environmental friendly formulation.⁴³

Following again a simple double encapsulation approach, essential oils are first caged in β -cyclodextrin to form inclusion complexes, and then encapsulated in silica using a water-based route making use of colloidal silica as a precursor of the silica matrix. Protected from the silica matrix, the essential oils become more resistant towards humidity, temperature and solar light. Progress highlighted in this account will hopefully assist research chemists and companies to accelerate the manufacture of new and more sustainable odorant and flavored materials based on flavor and fragrance species devoid of harmful effects. The latter species will be sol-gel entrapped in silica microparticles of different morphology and composition, from simple SiO_2 xerogels through composite polymer/silica materials or ORMSILs, targeting different applications.

Acknowledgements

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to Dr Chris Barbé, Ceramisphere, for sharing relevant information on sol-gel entrapped flavors and fragrances.

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