



Open challenges in sol-gel science and technology

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Abstract

Focusing on three different applications of sol-gel functional materials holding the potential to replace widely employed commercial products with significant economic and technical benefits, this study offers an original perspective on open challenges in sol-gel material science and technology. The applications discussed were selected on the basis of their societal and economic relevance and do not intend to represent the field of sol-gel material in general. The conclusions, however, are of general value and will hopefully aid young researchers and new companies to succeed in their efforts to commercialize chemical innovations based on sol-gel-derived functional materials.

Graphical Abstract



Keywords Sol-gel · Nanochemistry · Nanocoatings · Membrane · Silica · Bioeconomy

Highlights

- Focusing on three different applications of sol-gel functional materials, this study offers an original perspective on open challenges in sol-gel science and technology.
- Technical and economic obstacles have limited the industrial uptake of sol-gel functional products to replace conventional products generally based on polymers.
- For silica-based sol-gel functional products to become ubiquitous in fields today dominated by polymers, the direct route to obtain silicon alkoxides from waste organic (or inorganic) silica must be commercialized on large scale.

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1 Introduction

Collecting achievements in virtually all areas of sol-gel materials science and technology, *The Sol-Gel Handbook* edited by Levy and Zayat was published in 2015 [1].

Distributed in three volumes (“Synthesis and Processing”; “Characterization and Properties of Sol–Gel Materials”; “Application of Sol–Gel Materials”), the handbook’s 46 chapters provide readers with a comprehensive (1508 pages) treatment of the fundamental principles and a survey of the applications of sol–gel materials. Shortly afterward the second edition of the *Handbook of Sol–Gel Science and Technology* edited by Klein, Aparicio, and Jitianu [2] was published, following the 2005 first edition. Organized in three volumes (“Processing”, “Applications: Mechanical, Optical, Electrical, and Electrochemical”, “Applications: Preservation, Organic–Inorganic Hybrids, and Bio-related Materials”), the handbook includes 125 chapters, amounting to over 3780 pages. One is an interesting history of the chemistry and technology of sol–gel materials [3] that should be part of every course on sol–gel materials.

Three decades before, a truly impactful series of books in the field of sol–gel materials was the *Better Ceramics Through Chemistry* series (I through VII) containing the proceedings of a series of symposia organized every 2 years in the USA by the Materials Research Society between 1984 and 1996 [4].

Since 2015 two new volumes of the book series *Advances in Sol–Gel Derived Materials and Technologies* produced in collaboration with the International Sol–Gel Society to foster “an integrative approach to materials and technologies that are prepared and applied using the latest developments in sol–gel methods” have been published [5, 6], while another volume on the topic of optical and photonic sol–gel derived materials was published in late 2020 [7].

Readers are referred to the aforementioned texts for an updated and critical presentation of the main areas of contemporary research in functional sol–gel materials. Several other recent texts suitable for undergraduate students offering introductory knowledge have been updated lately to include technological advances and new applications emerging since the publication of the first editions in the 90s, including Pierre’s comprehensive introductory textbook [8] used in many graduate-level materials science courses.

This study offers an original perspective on open challenges in this prominent field of contemporary material science and nanotechnology selected on the basis of their societal and economic relevance.

Estimated to be \$2.2 billion in 2018 and forecast to increase to over \$5.2 billion by 2026 [9], thin films and coatings with optical, anti-reflection, photochromic, electrochromic, and magnetic functionalities, are by far the most important segment of sol–gel derived products. Potential applications of sol–gel materials, however, go much beyond coatings. In this respect, published data show evidence of a large unmet potential for sol–gel derived products, as well

as for truly large and global interest from industrial and academic researchers for sol–gel derived products. A search of a patent database in 16 different languages including English, Russian, Spanish, Danish, and Chinese filed between 2010 and 2020 returned 201,410 results [10]. A similar search encompassing patents in over 20 languages during the same decade gave over 30,000 inventors from industrial and academic research centers based in 56 countries [11].

Analyzing the global market of sol–gel derived products (coatings, includes catalysts, piezoelectric devices, and high-strength ceramics), recently market intelligence analysts identified a lack of investment in R&D and in resolving the high cost of raw materials as the two main constraints are hindering the growth of the market [12].

In the following, we focus on three application areas of sol–gel functional materials holding the potential to replace widely employed alternative commercial products whose industrial use, though, remains confined to a niche segment of the respective markets, namely textile sol–gel coatings, pervaporation membranes, and spherical catalysts. Selected, as mentioned above, on the basis of their societal and economic relevance these technologies do not intend to represent the field of sol–gel materials in general.

Obviously, the challenges identified in the following are not the only ones that must/can be solved through the creative use of sol–gel nanochemistry. One prominent example is in manufacturing all Li-ion battery components, including anode protective coatings and cathodes such as nanostructured LiFePO₄ powder for low cost and intrinsically safe Li-ion batteries [13]. Yet, the nature of the challenges to be faced is similar, and the forthcoming analysis and its conclusions can be generalized.

2 Textile nanocoatings

Along with Albo, we have recently clarified the controversy in the literature concerning the real industrial utilization of silica-based sol–gel nanocoatings by textile companies to produce high-performance textile fabrics endowed with new functional properties [14].

Böttcher et al. pioneered and successfully used silica nanosols to functionalize textiles and fibers [15] since the late 90s; however functional sol–gel coatings were not adopted by the German textile industry. In short, all coating systems based on tetraethoxysilane (TEOS) contain some significant fraction of ethyl alcohol, which cannot be removed from the coating solution, without causing quickly gelation. Unfortunately, no textile company in Germany had explosion-proof coating equipment (and a plant for burning alcohol), whereas if commercial aqueous nanosilica

sols were used, they did not form smooth transparent layers and adhered poorly to the fibers [14].

Technical advances in the formulation of waterborne silica-based nanosols and dramatically lowered production costs suggest that eventually sol-gel functionalized textiles will become ubiquitous.

Since then, advances in stabilizing the organically modified silica (ORMOSIL) nanosol, replacing ethanol in the water-based formulation with another co-solvent added in minimal amounts, have led to the introduction of waterborne ORMOSIL sol-gel formulations that can be purchased packaged in the sprayer and safely sprayed directly by consumers to provide all sorts of textile garments with lasting (wash-resistant) hydrophobicity 24 h after spraying. Two examples are the *Nano4-Textile* with >94% water and >6% silica content [16] or the *NewPro Nano Textile 4 NC* [17] respectively produced and commercialized across the world, by a Greek and a German company.

An insight into the current price of one such coating reveals the last key problem to be resolved prior to widespread industrial uptake of silica-based sol-gel coatings. The former *Nano4-Textile* waterborne coating is sold online (early 2021) at €102.47 for a 4 L batch, namely at €25.62/L [16]. The product does not need to be diluted prior to spraying, with optimal effect requiring 25–100 mL/m², depending on the fabric. Assuming one is willing to coat a textile article requiring the highest load, this means that coating 10 m² of fabric would cost >25€.

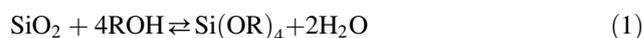
To learn if this cost is competitive, namely if customers in the profit-driven textile industry may be willing to buy it for mass production, one should consider that competing coatings companies supply similar waterproofing silicone coatings at a fraction of this price, because silicone is produced by the petrochemical industry (reacting chloromethane with silicon metal) at over 3 million t/a scale, growing at >10% yearly [18].

Cost reduction of the silanes precursors of xerogel coatings is the key requirement that once met, will drive the widespread uptake of sol-gel nanocoatings in the textile industry.

Produced via the hydrolytic polycondensation of Si alkoxides, the manufacturing cost of said coatings chiefly depends on the cost of silicon alkoxides. With the market entry of several TEOS manufacturers based in China in the first two decades of the 2000s, the price of TEOS has gone from over \$20/kg in 1990 [19] to \$2/kg today [20].

A further significant reduction in the price of TEOS is likely to originate from a new synthetic approach using different natural sources of SiO₂ as reported by Laine and co-workers when introducing the first version of the direct route from biogenic SiO₂ to TEOS in 2016 relying on the base-catalyzed depolymerization of SiO₂ with diols to form distillable spirocyclic alkoxysilanes and TEOS [21].

Shortly afterward, the process was advanced by Japanese researchers [22] who obtained TEOS in 70% yield by simply reacting in a 200 mL autoclave, 15 mmol of silica, in the presence of 10 mol% KOH (relative to silica) as a catalyst, and 100 mL of EtOH at 240 °C using 25 g of 3 Å molecular sieves. After 6 h, the yield of TEOS was 75%. Key to shifting the equilibrium reaction in Eq. (1) was the presence in an upper autoclave of 3 Å molecular sieves which promote the reaction between silica and ethanol towards the products by adsorbing water molecules vaporized from the reaction mixture.



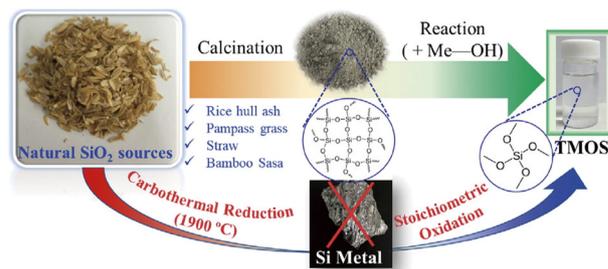
Further lowering the process cost, a simple treatment under vacuum at 300 °C regenerates the spent molecular sieves [22]. Recently, the team extended this approach based on water removal by using 2,2-dimethoxypropane as a dehydrant under carbon dioxide in the synthesis of tetramethoxysilane (TMOS) [23].

Rather than starting from expensive and toxic SiCl₄ and avoiding the need for expensive and cumbersome carbothermal reduction of silica (Scheme 1) the new synthesis of TEOS (or TMOS) starts directly from silica obtained from renewable inorganic biomass such as rice hull ash (RHA, an abundant by-product of rice production). Starting from RHA, silica with 2,2-dimethoxypropane at 240 °C for 24 h under 0.8 MPa CO₂ on a 1 L-scale reaction TMOS was obtained in 69% yield.

3 Pervaporation membranes

Widely explored by researchers at the Energy Research Center of the Netherlands in collaboration with the Universities of Twente and Amsterdam since their discovery in 2008 [24], the HybSi membrane technology was licensed for commercialization in 2010 to a Dutch company specializing in pervaporation membranes [25].

Comprised of an ORMOSIL thin coating of selective layer prepared by a sol-gel process from the bis-silyl



Scheme 1 One-step direct synthesis of TMOS by reaction of silica and methanol, using a base catalyst and acetal as a dehydrant under carbon dioxide. [Reproduced from Ref. [23], with kind permission]

precursors, such as BTESE [(EtO)₃Si-CH₂CH₂-Si(OEt)₃] cast on an Al₂O₃ tubular ceramic membrane support (the coating film is on the inside of the ceramic tube), these membranes can be used to purify various industrial solvents. For example, they can be used to increase productivity in biodiesel production (via water removal in the trans-esterification reaction) and in the dehydration of solvents like alcohols, ketones, aldehydes, aprotic solvents, organic acids, with significant improvements in product purity and significant savings in both CAPEX and OPEX when compared with conventional separation technologies like distillation [26].

As put by ten Elshof, the main difference between this new class of hybrid membranes and ORMOSIL with terminal organic groups (R-Si≡) lies in the fact that the hybrid membrane networks contain both ceramic ≡Si-O-Si≡ bonds and hydrolytically stable ≡Si-R-Si≡ bonds, with molecular-scale dispersion of both types of bonds [27]. From a structural viewpoint, 6≡Si-O-Si≡ groups need to be hydrolyzed by water molecules before an organosilica cluster dissolves and goes into a solution.

Contrary to currently commercialized polymer and silica and zeolite pervaporation membranes, the ORMOSIL-based membranes are stable in water at high temperatures, in aprotic and protic solvents, and in the presence of acids. This is not the case for polymer membranes that can be used at T up to ~100 °C with poor resistance against organic solvents and acids, and, for ceramic or zeolite A or zeolite T membranes, by their low hydrothermal and acid stability.

The sol-gel ORMOSIL technology can be successfully employed also in water desalination. For example, employed in a pervaporative distillation process the hydrophilic PV membrane HybSi PVM-039, comprised a proprietary cross-linked organosilane selective layer cast on an Al₂O₃ tubular ceramic membrane support, (tube exterior diameter of 10 mm, interior diameter of 7 mm, and length of 25 cm) was recently shown to be highly effective at desalting highly concentrated aqueous NaCl solutions (from 10 to 240 g/L) streams, consistently delivering <10 mg/L of dissolved solids in product water [28].

Similarly, in another application BTESE-derived membrane treated with concentrated (35%) aqueous HCl showed excellent pervaporation performance in the dehydration of an acetic acid/water (90/10 wt%) at 80 °C: separation factor up to 780 and flux (2.07 kg m⁻² h⁻¹), along with excellent stability within the investigated pervaporation time of 150 h at 80 °C [29].

In general, these silica-based hybrid membranes have a very long lifetime (up to 10 years), which provides further environmental benefits (of adopting this technology) due to the life cycle of the technology.

In 2001 on-site solvent recovery using pervaporation and vapor permeation was found to become standard practice in

the pharmaceutical and chemical industries [30]. Why, twenty years later, this technology has not replaced all other pervaporation membrane technologies such as those based on polydimethylsiloxane (PDMS) polymer or zeolites?

Once again, the answer lies in the higher cost, and longer payback period, when compared to polymeric membranes installed around the world in more than 150 industrial plants already in 2001 (with capacities between 20 kg/h to several tons per hour) regardless of “the prejudice which some engineers still have against the application of polymer membranes” [30].

The overall cost of a chemical process (*C*) to manufacture a chemical product, includes the production (*C_i*) and purification (*C_p*) process costs. Purification is either from unwanted by-products or from the process solvent:

$$C_{tot} = C_i + C_p \quad (1)$$

To reduce cost, a company will undertake all economically viable actions to reduce both terms of the equation above. Hence, it will for example adopt highly selective heterogeneous catalysis under-flow to eliminate unwanted by-products to achieve a lower *C_i* cost, and it will do the same by adopting new, lower-cost separation technology to reduce the *C_p* term in Eq.(1).

The payback time *T* (in years), namely the period of time required to recover the initial investment *I* requires generating an annual cash flow *C*, given by the ratio:

$$T = I/C \quad (2)$$

The investment faced by the company will only offer practical value if the cash flow (in terms of savings, in this case) is large enough to enable a quick return on investment. This time frame is 2 or 3 years in the case of the petrochemical industry. In the same industry energy efficiency even in 2009, shortly after the price of oil had reached its historic record in July 2008 (\$147/barrel), was found to have “a relatively low importance for innovation in chemical processes” [31].

Chinese and Japanese researchers recently wrote that in order “to make organosilica membranes commercially applicable”, based on their excellent flux and separation factors to dehydrate acetic acid mixtures “new protocols of calcination, precursor modification, and intermediate layer coating must be developed to reduce manufacturing costs” [32]. Such reduction of manufacturing cost invariably goes through a reduction in the price of the silicon alkoxide precursors, in this case, the BTESE bridged silsesquioxane whose cost (on laboratory scale) for 96% pure product exceeded €600/L by early 2021 [33].

In other words, to compete with low-cost polymers used in conventional pervaporation membranes, the production of sol-gel pervaporation membranes needs to start from Si alkoxides of substantially lower cost, which can be achieved

only by replacing their current syntheses from metallic silicon sourced from quartz.

As put by Laine et al. [21], silicon in the form of silica makes up more than 40% of the earth's crust, but its use as chemical raw material so far has relied exclusively on the equipment and energy-intensive carbothermal reduction of quartz SiO_2 carried out at 1900 °C (requiring some 140 MWh/t of energy). Such conditions are needed because silicon is the kinetic product whereas SiC is the thermodynamic product. Thus, the first step is always a CO_2 -intensive process often overlooked in efforts to provide the petrochemical, photovoltaic, and semiconductor industries with the raw material (SiCl_4) needed for the production of silicone polymers as well as of “electronic-grade” and “solar-grade” silicon of exceptionally high purity.

The new one-pot process affording Si alkoxides starting from biogenic or mineral SiO_2 [21–23] entirely by-passes the need of SiCl_4 obtained from silicon derived by the carbothermal reduction of quartz, enabling the commercialization of numerous technologies based on sol–gel derived silica and organosilica products so far limited by the high cost of silicon and organosilicon alkoxides.

Though generally overlooked in the literature, the high cost of silicon alkoxides limiting the uptake of sol–gel derived silica-based materials have been reported by scholars in Finland in 2009 [34]. To synthesize high-quality periodic mesoporous silicas, rather than commercial TEOS, the team successfully used an amorphous multicomponent metal oxide dissolved in concentrated (2 M) formic acid as the silica source.

Similarly, reviewing numerous works in which low-cost inorganic or organic waste has been used as an alternative precursor for the synthesis of silica aerogels, researchers in Turkey recently emphasized how the high cost of silicon alkoxides has limited industrial production of polymer composites including silica aerogels or xerogels [35].

4 Spherical solid catalysts

Describing the successful multigram, solvent-free full hydrogenation of impure (82% purity) squalene to squalane under solvent-free and mild reaction conditions of 0.5 mol% Pd, 3 bar H_2 , and 150 °C, the first spherical sol–gel entrapped catalyst was introduced in 2017 [36]. Smoothly reused in eight consecutive cycles, with <2 ppm levels of Pd leaching in solution, the catalyst opened the route to sustainable manufacture of the best emollient known in the cosmetic industry via hydrogenation of impure squalene obtained from vegetable sources (olive oil distillate by-product or via sugar fermentation over genetically modified bacteria). Significant economic, environmental, and health benefits originate from this innovation enabled by a sol–gel

catalyst because prior to then most squalane had been produced via hydrogenation of squalene extracted from shark liver oil over Ni-based heterogeneous catalysts leaching plentiful toxic nickel in solution [37].

Besides the large open mesoporosity, and hydrophobicity of the organosilica matrix protecting the palladium nanoparticles tightly entrapped within the sol–gel cages, the high selective catalytic activity of the newly developed spherical catalyst was ascribed to the spherical morphology. This morphology enables a much larger surface-to-volume ratio when compared with analogous sol–gel catalyst comprising irregular xerogel microparticles.

Indeed, shortly afterward, the new catalyst was successfully applied to multigram hydrogenolysis of aromatic alcohols, aldehyde, and ketones under even milder conditions (0.1 mol % Pd, 1–3 bar H_2 pressure, 70–100 °C) [38].

Made of Pd nanoparticles encapsulated within a spherical mesoporous ORMOSIL matrix, the catalyst is obtained via a template-driven sol–gel process [39] that can be easily scaled up fully retaining the spherical morphology of the microparticles (Fig. 1) comprising the catalyst embedding 3.1 nm Pd nanocrystals.

The catalytic material is so effective that it selectively mediates the hydrogenolysis of 4-carboxybenzaldehyde, an abundant by-product in the terephthalic acid synthesis, to *p*-toluic acid at 100 °C under 3 bar H_2 . This contrasts with previous state-of-the-art catalysts Pd–Ru/C employed for the hydro purification of terephthalic acid requiring 14 bar H_2 at 250–270 °C [40].

When compared to conventional catalysts such as Pd/C or Pt/C, these spherically shaped hydrophobic sol–gel oxides functionalized with noble metal nanoparticles are far

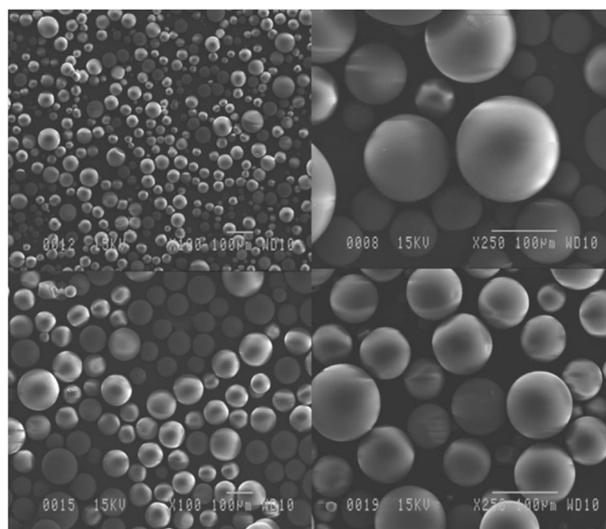


Fig. 1 SEM images at 100 and 250× magnification of SiliaCat Pd(0), $d_{50} = 100 \mu\text{m}$. Lab-scale synthesis (top) and 1.6 kg scaled-up synthesis (bottom). [Reproduced from Ref. 38, Creative Commons CC BY-NC-ND 4.0 license]

superior in reactions as important as olefin hydrosilylation under solvent-free conditions used in the manufacture of valued organosilicon compounds [41]. Furthermore, they can be employed in continuous processes which are of direct relevance not only to the petrochemical industry but now also to the fine and specialty chemical industry.

For instance, the stability of the new catalysts, as opposed to the poor stability of Pd/C recently led researchers at a catalysis company to identify the excellent performance of a ceramic (i.e., metal oxide) functionalized with Pd nanoparticles 3D printed as a foam in the continuous hydrogenation of squalene, even though under harsher conditions (25 bar H₂, and 240 °C) with the squalene feed dissolved at 75 wt% in the organic solvent [42].

The latter findings are of high relevance to the fine chemical industry wherein selective hydrogenation using supported metal catalysts is a key conversion generally carried out in over 1000 L batch reactors requiring catalyst washing in between cycles to slow down deactivation, and a costly purification process of the hydrogenated reaction product from residual toxic Ni leached in solution. For comparison, a continuous system using a 50 L flow reactor is able to replace a 1500 L batch reactor producing 20 t of squalene per month [42].

Even in irregular microparticle geometry, the organosilica-entrapped Pd catalyst *SiliaCat* Pd(0) selectively mediates the partial hydrogenation of vegetable oils dissolved in an organic solvent under hydrogen balloon room temperature conditions with no *cis/trans* isomerization, retaining its selective activity even after multiple reaction cycles [43]. Hence, the findings above concerning spherical sol-gel catalysts usable under solvent-free conditions may have opened the route to long-awaited hardened fats free of undesirable *trans*-fats.

In general, heterogeneous catalysis under-flow is an underutilized powerful tool in the fine chemical industry [44]. Employed in flow catalytic processes new generation sol-gel catalysts including the aforementioned spherical catalytic materials, streamline and improve a variety of key processes used by the fine chemical industry [45].

Along with Luque, we have lately suggested that the primary reason for the poor uptake of heterogeneous nanocatalysis underflow is educational: the industry lacks sufficient young researchers proficient in flow chemistry and nanocatalysis [46]. This, in its turn, requires filling this widespread gap in chemistry education by reshaping education in catalysis [47].

5 Conclusions

Different obstacles of different nature, technical or economic, have limited the industrial uptake of sol-gel

functional products to replace the corresponding conventional products generally based on polymers.

In the case of textile finishings, we had to wait for advances in the formulation of waterborne silica-based nanosols to face the lack of explosion-proof textile coating equipment and of plants for burning alcohol originating from the hydrolysis of the first generation nanosols based on mixtures of TEOS and organically modified Si alkoxides.

In the case of pervaporation membranes, the expensive cost of silicon alkoxides has been the main obstacle to industrial uptake of sol-gel hybrid silica membranes of distinctly better performance when compared to lower-cost polymeric membranes.

In high-end applications such as cosmetic sunscreens [48], catalysts [49] and reagents [50] for fine chemical productions, and even more pharmaceuticals [51], the expensive cost of Si alkoxides is not an issue because most of the value, the intellectual property, now is incorporated in the price of the formulated product (cosmetic or pharmaceutical product, packaged catalyst or reagent) in which the sol-gel functional material is the active ingredient.

For silica-based sol-gel functional products to become ubiquitous in fields today dominated by polymers such as coatings, membranes, and resins for 3D printing, the Laine's process to obtain silicon alkoxides from waste organic (or inorganic) silica [21] must be commercialized on large scale.

Asked to comment, Laine added:

“You are completely correct, indeed, we are exploring this very option to make high purity precipitated silica with a very large commercial entity at present [52].”

Compared to quartz, biogenic feedstocks such as rice hull (husk) offer higher purity from the start. After burning it to generate heat and electricity, the residual rice hull ash comprised of 90% amorphous silica currently disposed of as waste by rice companies is ready to be converted into TEOS at a fraction of the cost of the synthesis starting from metallic Si. Manufacturing of biobased TEOS or TMOS is even made cheaper by carrying out the process under-flow [22] or using a base catalyst under a CO₂ atmosphere [23].

The chemical industry is about to be reshaped by powerful societal megatrends concerning the environment, health, and energy which permeate society on a global scale [53]. These trends are likely to drive soon the emergence of distributed chemical productions using lean and green chemical processes starting from biological resources.

Publishing the first base-catalyzed depolymerization of SiO₂ assisted by glycols Laine and co-workers wrote that their process can be seen “as the culmination of over 85 years of effort targeting the same or similar objectives [21]”. The new process and those using simple ethanol and

methanol alcohols [22, 23] are ready to be industrialized. They are easily and quickly scalable to meet large demand, with virtually no technical or economic obstacles. This will lead to a dramatic reduction in cost and a similarly high rise in the supply of both TEOS and TMOS, which will translate into similar price reductions of the organically modified silanes whose industrial manufacturing starts from the above basic silanes.

Eventually, this will unleash the applicative potential of sol-gel-derived functional products which so far has remained a niche industry. For comparison, even its largest segment comprised of protective coatings, after more than three decades since the inception of the first sol-gel silica-based coatings in the early 1980s, is not even worth \$3 billion [54].

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Author contributions RC and MP conceived the study. MP wrote the first draft of this study. RC reviewed the manuscript.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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