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Topical Review

The void side of silica: surveying optical properties and applications of mesoporous silica

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Abstract

Mesoporous silica stands out as a remarkable, low-density transparent material characterized by well-defined nanometric pore sizes. It is available in various morphologies, including monoliths, nanoparticles, and films. This material plays a pivotal role in numerous technological applications, both independently and as a component in hybrid composites, acting as a host for a diverse range of inorganic and organic materials. Among the synthetic routes, we accounted for the sol-gel method because of its large success in producing both nanoparticles and bulk mesoporous silica. This review focuses on exploring the optical properties of mesoporous silica and mesoporous silica-based composites, delving into how the huge void space within mesoporous silica can be harnessed across various fields: thermal and electrical insulations, photonics, environmental devices, or nanocargos for drugs and bioimaging. This comprehensive examination underscores the multifaceted potential of mesoporous silica, positioning it as a key player in the development of innovative solutions across various scientific domains.

Keywords: mesoporous silica, optical properties, hybrid composites, nanosystems, porous materials

1. Introduction

Mesoporous Silica (MS) is a low-density transparent material with nanometric porosity ranging from 2 to 50 nm, according to the IUPAC definition [1]. The mild synthesis conditions of sol-gel methods [2] allow the production of MS in the form of monolith, nanoparticles, and films with controlled size, porosity, morphology, and high chemical stability. Besides

the characterization of the structure and morphology of the material and the investigation of the mechanical, thermal, and optical properties of MS by itself [3, 4], the research has been mainly related to the exploitation of MS as a host [5]. Indeed, thanks to its chemical inertness and low toxicity the huge void space within the porous silica matrix offers a unique technological advantage in engineering new composite materials, through the incorporation, by means of physical or chemical confinement, of molecules and surface groups for functionalization. Cost-effective mass production, lately spread by the manufacturing from ash sources [6], is a further benefit that promoted in the last decades the investigation of MS-based systems high-tech applications. A search on the Scopus database on the terms MS and MS nanoparticles (MSNs) shows that the number of papers keeps almost linearly increasing by

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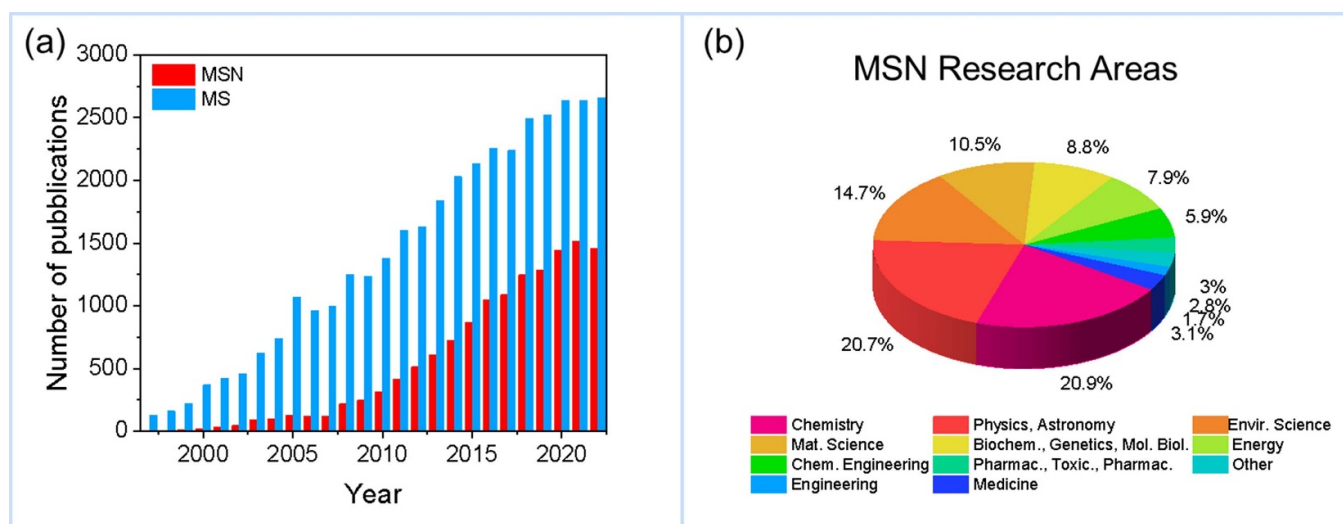


Figure 1. Number of publications of MS and MSN (a) and Research areas of MSN (b) as gathered from Scopus database (data extracted in June/2023).

500 per year, the research areas spanning from physics and chemistry to medicine and environmental science, the boundary being difficult to mark sometimes (figure 1). The proposed applications regard a lot of technological fields, from catalysis to photonics and biomedical applications, encompassing anticorrosive agents [7], strengthening of textiles [8], adsorbents for humidity and pollutants [9], thermal insulating glasses [4], insulating layers for microelectronics [10], sensing [11], drug delivery [12] and cell imaging [13]. In the last 20 yr, our research group was involved in the investigation of the optical properties of MS and its exploitation to prepare some composites where the structural and morphological properties of the silica host matrix could help in promoting, tuning, or selecting specific properties of the guest.

In this review we briefly summarize how MS can be prepared, what are the structure and morphology of different silica matrices and how these features can be used for specific applications through functionalization and engineering of the MS features. We discuss first how disordered and ordered MS can be prepared in the form of nanoparticles, monoliths, or films by means of the sol-gel technique, tailoring the structural and morphological properties by changing the parameters of the synthesis (section 2). Then we consider the applications of MS *per se* or as a host in hybrid compounds (section 3). Focusing on the optical features, we consider how the optical and thermal properties of MS promoted its exploitation as UV-shielding insulating material for space applications or to produce transparent windows with very low thermal conductivity. Further applications in photonics also account for pollution sensing, manufacturing photonic crystals (PC), or emitting devices. Taking into account the large void volume within the material we look at the applications of MS for environmental purposes and catalysis. Finally, we consider how, by filling the void with specific chemical moieties, one can introduce desired functionalities for thermoelectric applications,

photonics, bio-imaging, bio-sensing, or drug delivery. The last section is dedicated to considering future perspectives and open issues that could further spread the applications of MS in real life.

2. Synthesis and features of MS

2.1. Synthesis of MS

Besides the various synthetic approaches to produce MS [14, 15], the two most common ones are the sol-gel method and the microemulsion technique [16]. We considered mainly sol-gel prepared MS for two reasons: the first one is that by sol-gel method is possible to prepare nanoparticles and bulk materials, both in the form of monoliths and films, as reported in the following sections. The second one is that it allows to easily introduce chemical moieties within the MS matrix during the synthesis process to functionalize the material for specific applications.

The sol-gel method was developed during the late 1970's, and it regards a low-temperature synthesis of chemical precursors through hydrolyzation and polymerization reactions that lead to wet gels and, after removal of the solvent, to compaction into a porous matrix. In the case of MS, the starting solution contains a silicon alkoxide, typically tetraethyl orthosilicate (TEOS), and porous matrices made of only 5% of SiO₂ and 95% of air can be obtained in the form of xerogel or aerogel depending on the solvent extraction. The synthesis allows to control the chemical composition and the microstructure, leading to a transparent material of very high mechanical strength and very low thermal conductivity. By means of the famous Stober's method, which underwent an incredible renaissance in the last decades, uniform, monodispersed silica particles can be prepared with size and surface properties customizable on purpose [17].

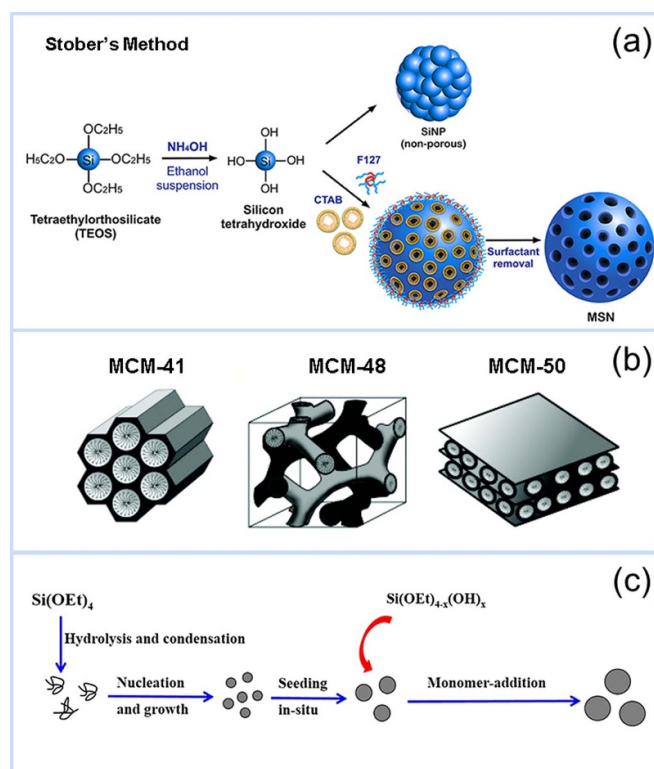


Figure 2. (a) Stober's method. Reproduced from [16]. CC BY 4.0. (b) Structures of various MS. Reproduced from [7] with permission from the Royal Society of Chemistry. (c) Formation process of MSN. Reprinted with permission from [18]. Copyright (2017) American Chemical Society.

Table 1. Structural and morphological characteristics of various MSN. List of acronyms: MCM-Mobil Crystalline Materials; SBA- Santa Barbara Amorphous; FDU—Fairleigh Dickinson University; KIT- Korea Advanced Institute of Science and Technology, COK- Centre for Research Chemistry and Catalysis.

	Pore symmetry	Pore size (nm)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Specific surface area ($\text{m}^2 \text{g}^{-1}$)	References
MCM-41	2D hexagonal $P6mm$	1.5–8	>1.0	>1000	[19]
MCM-48	3D cubic $Ia3d$	2–5	>1.0	>1000	[20]
MCM-50	Lamellar $p2$	2–5	>1.0	>1000	[21]
SBA-11	3D cubic $Pm3m$	2.1–3.6	0.68	>1000	[22]
SBA-12	3D hexagonal $P63/mmc$	3.8	0.62	932	[23]
SBA-15	2D hexagonal $P6mm$	6–10	1.17	600–900	[24]
SBA-16	Cubic $Im3m$	2.7–3.7	0.4–0.7	700–1000	[25]
FDU-16	Cubic $Fm3m$	10.0–12.4	0.66–0.86	280–712	[26]
KIT-5	Cubic $Fm3m$	9.3	0.45	715	[27]
COK-12	Hexagonal $P6mm$	5.8	0.45	420–550	[28]

The sol–gel process can be tuned to obtain also ordered structures, through the modified Stober's method (figure 2(a)) [16]. The first report of ordered MS was obtained by Mobil Oil Corp. in 1992, and from the company derives the name Mobil Crystalline Material, known as MCM-41. Other well-known acronyms refer also to the accredited first producer, like SBA to Santa Barbara Amorphous made by Santa Barbara University, or FDU from Fairleigh Dickinson University [14]. Indeed, different morphologies and textures can be realized (figure 2(b)) from well-separated aligned pores as in the hexagonal structures of SBA-15 and MCM-41 to lamellar mesostructures of MCM-50 or interconnected disordered porous systems like body-centered and face-centered cubic

MCM-48, SBA-16 and FDU-12. Table 1 reports the main features of various MSN.

The sol–gel synthesis starts from the hydrolysis of an alkoxy silane precursor, like TEOS, to produce a hydrolyzed silane. The silanol groups undergo condensation and through polymerization branched siloxane clusters are obtained. The latter can ignite the nucleation of nanometric seeds to produce silica gel or silica nanoparticles by adjusting the pH of the solution. One can think that since the synthesis has been known for almost 50 yr the whole process is well-established. However, only recently the kinetics of the nanoparticle assembly has been finally understood [18], calling for the nucleation of small nanoparticles from silanol monomers,

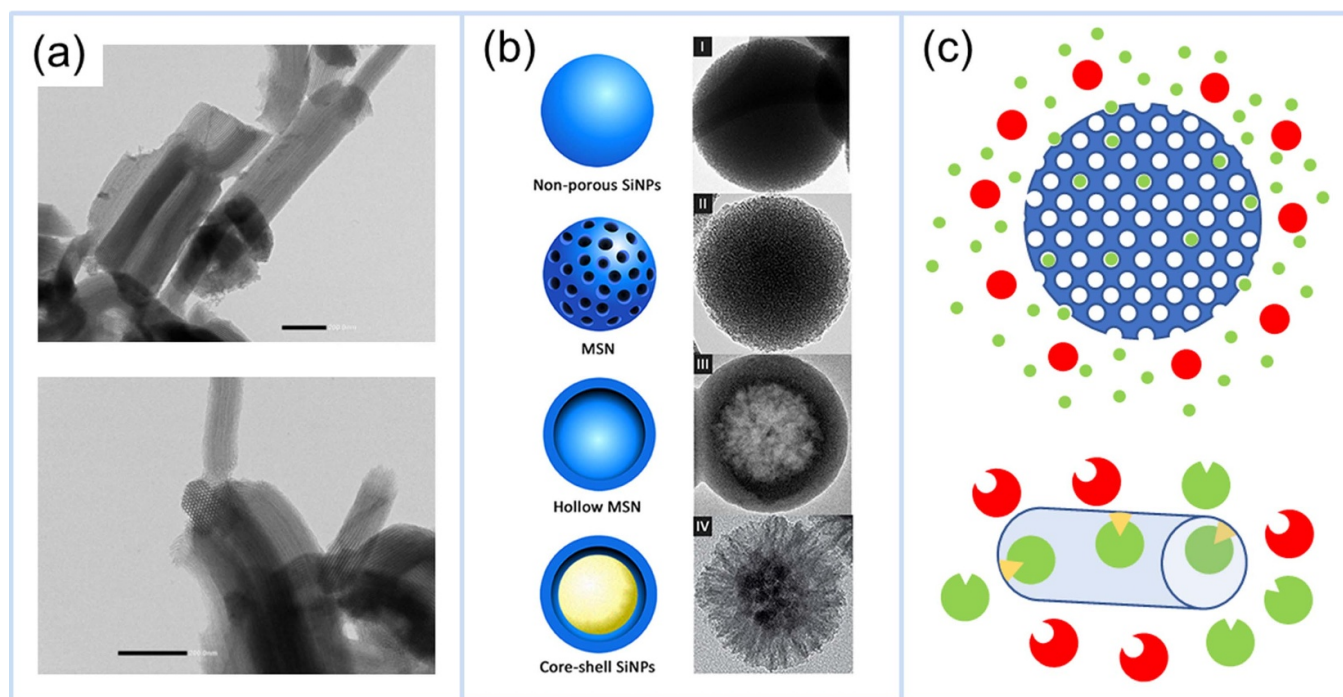


Figure 3. (a) TEM images of SBA-15. (b) Schematic representations of different silica nanoparticles with respective TEM images. Reproduced from [30]. CC BY 4.0. (c) Size selectivity and surface selectivity of the porous silica surface.

followed by the formation of a siloxane network and finally by the increase of these seeds by further addition of silanol monomers (seeded growth) (figure 2(c)).

All MS have a very large specific surface area (SSA), up above $1000 \text{ m}^2 \text{ g}^{-1}$, very reduced mass density, and pore size in the mesoporous range [7]. Figure 3(a) reports the transmission electron microscopy (TEM) images of an SBA-15 commercial sample (Sigma-Aldrich) with a pore diameter of 8 nm in a highly ordered, two-dimensional hexagonal structure.

By changing the sol-gel synthesis conditions, in particular by controlling the pH, one can easily obtain gel for the preparation of monolith or film of MS or the nucleation of nanoparticles (MSN) [29]. The latter are produced as ordered MS mainly through the modified Stober synthesis where a proper surfactant is exploited as a template. The same sol-gel synthetic route can be followed to obtain non-porous nanoparticles, hollow MSN, or core-shell Silica Nanoparticles (figure 3(b)) [16]. Among them, in this paper, we will consider only MSN. When the synthesis is finished, one obtains bulk silica walls of a few nanometers (1–2 nm) [19] and a pore surface with siloxane and silanol groups. The latter ones allow modifying the surface with specific chemical moieties and introducing desired functionalities into the silica matrix by non-covalent or covalent bonding of specific molecules to the MS surface. At the end of the synthesis, one gets a porous matrix able to selectively adsorb various species from the environment, selecting them by size or by specific interaction with the pore surface previously modified on purpose (figure 3(c)).

2.2. Features of MS for technological applications

MS nanoparticles have shown to have excellent properties for various technological applications, from bioimaging to photonics and thermoelectric. As pictured in figure 4, the relevant features that make MS an unicum in the panorama of porous materials are the large SSA and the pore volume, the pore size which can be adjusted in the 2–50 nm range and organized in different ordered or disordered texture, the reactivity of the silica surface. In the case of nanoparticles, further important properties are the particle size tunable from a few to hundreds of nanometers, and the good dispersion in solution. All the applications listed in the figure and reported in section 3 exploit to some extent all the features reported, and a specific feature can be most relevant in different fields. For example, the dimensions of the MSNs are mainly relevant for biomedical applications, to ensure endocytosis by living cells allowing bioimaging or drug delivery depending on the loading of MSN for selected purposes. The size of particles is also relevant for photonic applications, to tune the photonic gap in photonic crystal (PC). The pore size is a feature that allows to control the loading of specific species, reported as a separated technological goal because it is crosscutting and relevant to the other fields. Indeed, selectivity in loading is a required characteristic for environmental remediation, drug delivery, sensors, and photonics. Loading is also related to large SSA of MS, allowing the introduction of a high concentration of specific drugs or dyes into the MS matrix for medical therapy, bioimaging, lightning, or potential solid-state laser media.

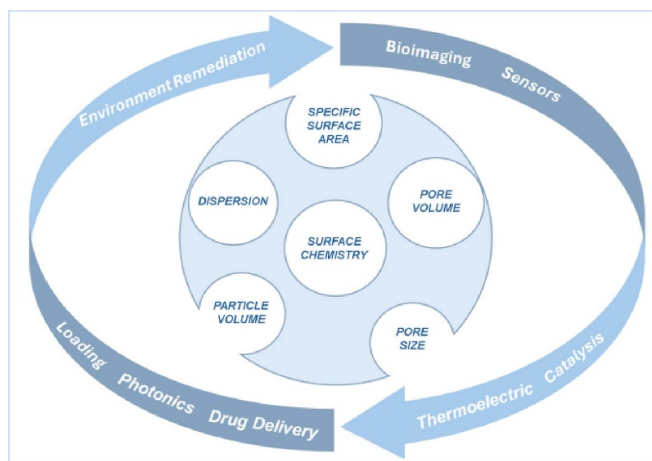


Figure 4. Specific features and applications of MS.

Thermoelectric, catalysis, and environmental remediation also take advantage of pore size and SSA, paired with the texture and topology of the porosity. As for the pore volume, it is the main parameter in regulating the size of the silica skeleton, thus affecting the biodegradation of MS for biomedical applications. Surface termination of MS by silanol groups allows easy functionalization to increase loading selectivity, control concentration phenomena, or provide stimulus-responsive functionalities to the material. It also allows controlling dispersion of MSN in solution, well-suspended NPs being mandatory for biological applications. In table 2 we list the works we reviewed in the following section by reporting the features of MS type and the observed properties to test the selected applications.

3. Applications of MS

3.1. MS on space

The number of proposed applications for MS is large and constantly increasing and many reviews are focusing on specific ones. In this paper, we want to give an overview of such a huge panorama, with a slight focus on the applications involving optical properties because of our involvement in this research field. In general, almost all applications consider MSN-based systems, since MSN are easier to prepare than large monolith aerogel samples. The critical point is the extraction of the solvent because it may lead to the formation of cracks, thus limiting the macroscopic size of the samples. However, samples as large as 10 cm in size have been prepared such as the ones applied to shield the photovoltaic panel of the Mars Rover, or the ones used to collect stardust powders following a comet in the late 1990 on a NASA space mission. In those cases, MS was selected because of its optical transparency, low thermal conductivity, reduced mass density, and porosity. Those are ideal features for space applications, as recently proposed in view of a possible human life on Mars [48]. Indeed, accounting for the extreme environmental conditions on Mars in terms of low temperatures and high UV irradiation, life cannot survive on the red planet unless its atmosphere is

changed to allow the greenhouse effect to increase the temperature and shield UV irradiation. From a conceptual point of view, the application of a 2–3 cm-thick layer of silica aerogel placed over sufficiently ice-rich regions of the Martian surface could solve the problem. Such a transparent shield will simultaneously transmit sufficient visible light for photosynthesis, block hazardous ultraviolet radiation, and raise temperatures underneath it above the melting point of water. By mimicking the Martian conditions, it was experimentally shown that such an MS layer made by particles or tiles allows increasing the temperature of about 50 K and largely reduces the transmitted UV radiation. Thus, the porous silica-based greenhouse solid state effect could self-sustain life on Mars.

3.2. Environmental applications

The large porosity of MS materials calls for applications in the environmental field, to remove pollutants from air or water. Nanoparticles of MS have shown good performances in capturing volatile organic compounds (VOCs) from the ambient or organic molecules, such as dyes or oil, from the aqueous phase [44]. In the case of oil and salt-water mixtures, CF₃-modified aerogels were able to cleanly separate the oil from the water, showing a capacity of the CF₃-aerogels mixtures as high as 237 parts of oil to 1 part of aerogel [44]. Despite the possibility of designing membranes blending MS nanoparticles, it would be preferable to produce MS monolith because of the easy handling and recovery of the blots after use. It was reported that MS monolith with surface area in the 500–850 m² g⁻¹ range and a total pore volume of 1.1–1.2 cm³ g⁻¹ are suitable adsorbents of organic pollutants in water or VOCs in the gaseous phase, their performances being comparable to the ones of the reference MS nanoparticles [9]. We recently prepared some monoliths of silica aerogel in the shape of discs of about 2 cm in diameter and 0.5 cm in thickness exploitable in recovering oil spilled at sea [45]. Indeed, when environmental remediation is the target, one needs sorbents with high and stable oleophilic features paired with hydrophobic properties. Reduced graphene oxide (rGO) nanostructures were incorporated into silica aerogels by means

Table 2. List of MS types and MS-based systems categorized by applications. The table highlights the MS main features relevant to the investigated application and the relevant properties of the MS-based systems. MS features acronyms: PS = pore size, PD = particle dimensions, PV = pore volume, SSA = specific surface area, D = dispersion, SC = surface chemistry. System acronyms: MS = mesoporous silica, MSN = mesoporous silica nanoparticles, rGO = reduced graphene oxide, CDs = carbon dots, PEDOT = poly(3,4-ethylenedioxythiophene), PBA = phenylboronic acid.

Application	MS type	MS main features	MS-based system	MS-based system property	Reference
Loading	MS monolith	SSA	Void MS	Raman, Photoluminescence	[31, 32]
	MS monolith	SSA	MS/Dye	Photoluminescence	[33–43]
Environment remediation	SBA-15, MCM-41	PS	MSN/miscellanea	VOC removal, CO ₂ capture	[44]
	MS monolith	PS, SSA	MS/rGO	Oil sorption	[45]
Catalysis	SBA-15, MCM-41	PS, SSA	MSN/miscellanea	CO reduction	[44]
	MSN, SBA-15, SBA-16, MCM-41, SBA-16, MS monolith	PS, SSA	MSN/miscellanea	Catalytic reactions	[46]
	MS monolith	PS, PV	MS/Co, MS/Fe	Paramagnetic features	[47]
Optical window	MS monolith	PS, PV	MS/organosilica	Optical transmission, thermal conductivity	[4]
	MSN, MS monolith	PV	Void MS and, MSN	Optical transmission, thermal conductivity	[48]
Photonics	MS monolith, MSN	SSA	Void MS and MSN MS, MSN	Photoluminescence	[49–51]
	MSN	PD	Void MSN	Photonic Crystal	[52, 53]
	MS, MSN	SSA	MS/Dye, MSN/Dye	Photoluminescence	[54–63]
	MS film, MSN	D, SC	MS/CDs	Photoluminescence, LEDs	[64–66]
Sensors	MS monolith	PS, PV, D	MS/CDs	Photoluminescence	[67]
	SBA-15, MCM-48	PS, D, SC	MS/CDs	Tunable photoluminescence	[68, 69]
Sensors	MS film, MSN	SSA, PV	MS or MSN/miscellanea	Photoluminescence, Raman	[70]
	MS monolith	PS, SSA	Void MS	Photoluminescence	[71–74]
Thermoelectric	SBA-15, MCM-41	PS	MSN/Bi ₂ Te ₃	Thermal/electric conductivity	[75]
	MCM-41	PS, PD	MSN/Nb-SrTiO ₃	Thermal/electric conductivity	[76]
	MSN	PD	MSN/Carbon	Thermal/electric conductivity	[77]
	SBA-15	PS	MSN/PEDOT	Electric conductivity	[78]
Biomedical field	MSN	PS, SC	MSN/miscellanea	Drug delivery, bioimaging	[14, 79]
	MSN	D, SC	MSN/CDs	Tunable photoluminescence	[80]
	MSN	PS, SSA	MSN/ReS ₂	Drug delivery	[81]
	MSN	SC, SSA	MSN/Dye	Drug delivery, bioimaging	[82, 83]
	MSN	SC	MSN/aptasensors	Biosensing	[84]
	MS film	SC	MSN/miscellanea	Biosensing	[85]
	MS film	SC	MSN/PBA	Biosensing	[86]

of a one-pot sol–gel method based on the co-gelation of TEOS as the silica precursor and GO. Nanocomposites displayed a homogeneous distribution of rGO within MS textures up to 15 wt% loading. The composite rGO-SiO₂ aerogels were able to oil sorption of ~7–11 times the mass of the sorbent. The presence of rGO nanostructures increased

the sorption features as compared to the raw MS system and provided the nanocomposites with the required selectivity toward oil sorption rather than water. In addition, the composites showed durable hydrophobicity and recoverability after oil burning, thus providing a longer shelf-life than pure MS silica adsorbents.

Another relevant environmental issue is to detect the presence of a specific hazardous agent in the analyzed ambient, such as Cu^{2+} , Co^{2+} , Hg^{2+} , Nitric Oxide, TNT, or bacteria, to cite a few. A recent review by Kong and co-workers extensively reports the achievement of MS-based optical heterostructures for sensing applications [70]. By filling the voids of silica porous matrices with fluorophores or photosensitizer units, various heterostructures can be implemented with different fabrication methodologies for selected sensing applications. The hybrid heterostructures can be assembled in manifold architectures through covalent or non-covalent interaction of sensing units to the silica surface, including ions, molecules and macromolecules, metal complexes, and nanoparticles. Because of its sensitivity and specificity to analytes, fluorescence is the optical property usually involved in the sensing mechanism, allowing turn-on/off of the emission or ratiometric evaluation of the fluorescence variation; sometimes absorption, transmission, or Raman spectroscopy is also applied to estimate the concentration of the detect agent.

3.3. Catalysis

Another relevant field of application for MS is catalysis where the interconnected mesoporosity of the material can be exploited to catalyze a mass flow of reactants. There are various reports on the applications of MSN in the field of heterogeneous catalysis [87, 88] exploiting the relatively large pores for efficient mass transfer and the easily functionalizable high surface area for a high concentration of active sites [46]. Despite some limits in providing the acid/base functionalities and in promoting the acid or base-catalyzed side of reactions, it was reported that channel connectivity and length of MS are relevant issues since also the morphology of porosity could be a critical parameter to enhance catalytic performance [44].

However, as far as monoliths are concerned, the main issue is still the preparation of large crack-free mesostructured silica membranes. Recently, we investigated the production of highly ordered SBA-16 mesoporous nanocomposites aiming at providing easy accessibility and diffusion in all directions for catalytic processes [47]. Indeed, as compared to the ordered hexagonal 2D matrix of MS like MCM-41 or SBA-15 where the parallel pores are accessible only in one direction, SBA-16 is a 3D cage-like system of interconnected pores that produces a cubic array accessible by all directions. This matrix can support metallic nanoparticles preventing their agglomeration and coalescence eventually providing augmented selectivity in catalysis through size selection of reactants and/or products. We have been successful in preparing composites with sizes up to 10 cm (figure 5(a)) with cm scale dimensions even after calcination and reduction at high temperature. The samples were doped with Co or Fe–Co co-doping, which aggregates as 10 nm of face-centered (fcc) nanoparticles within the ordered structure of SBA-16 silica (figure 5(b)) as also confirmed by optical absorption measurements. The magnetic properties of the composites were measured as a function of temperature and applied magnetic field (figures 5(c) and (d)) showing that superparamagnetic membranes are indeed formed. The difference between the

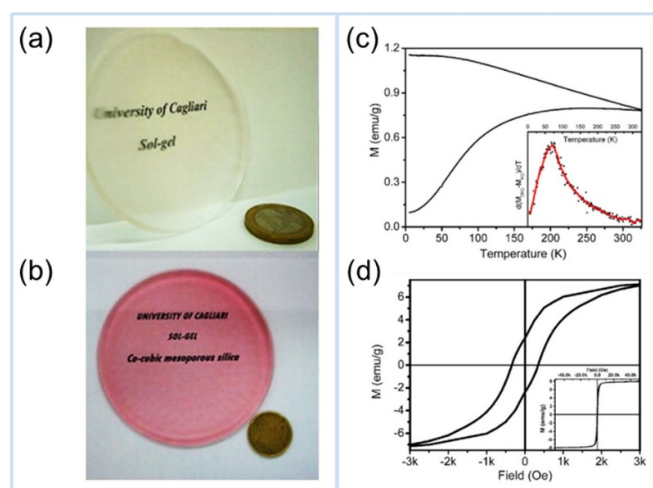


Figure 5. (a) Raw and (b) co-doped SBA-16 monoliths. (c) Magnetization of co-doped SBA-16 vs temperature and (d) magnetization vs magnetic field. Reprinted from [47], Copyright (2014), with permission from Elsevier.

maximum temperature in the zero field cooling (ZFC) procedure (250 K) and the peak in the first derivative of the magnetization signal (72 K) is a clear indication that the interparticle interactions among Co and Fe–Co NPs in MS host play a fundamental role in increasing the overall anisotropy energy barrier of the sample. As compared to bulk materials, the variation in the anisotropy should be attributed to interparticle dipole–dipole interactions, which are strongly influenced by the disordered distribution of nanoparticles within the silica matrix. The saturation magnetization and the ratio between remnant magnetization and saturation magnetization deduced from the hysteresis loop (figure 5(d)) confirmed the observed distribution within the Co-MS composite where the Co nanoparticles could promote the catalysis and allow recovering of the membrane at the end of the process by means of magnetic interaction.

3.4. Exploiting optical properties of void MS

Soon after the discovery of the ordered and size-controlled MS, there was a large interest in the optical properties of the materials by itself, looking at their relationship with the morphology of the porous systems, the pore size, and the presence of specific groups at the surface, like OH. Indeed, the changes in the optical transmission could be exploited for environmental sensing or should be prevented in the case of thermal isolating transparent window applications. Also, the emission features, related to the natural passivation of the silica surface, are quite sensitive to the environment, thus fostering the research on the optical features of void MS. The natural benchmark was bulk silica and the plethora of point defects producing optical absorption and emission fingerprints [89, 90], eventually related to laser or high energy irradiation [91, 92]. Another obviously occurring reference is nanosized silicon [93, 94] since silicon nanocrystals and porous silicon have their surface layer typically oxidized. It was indeed reported

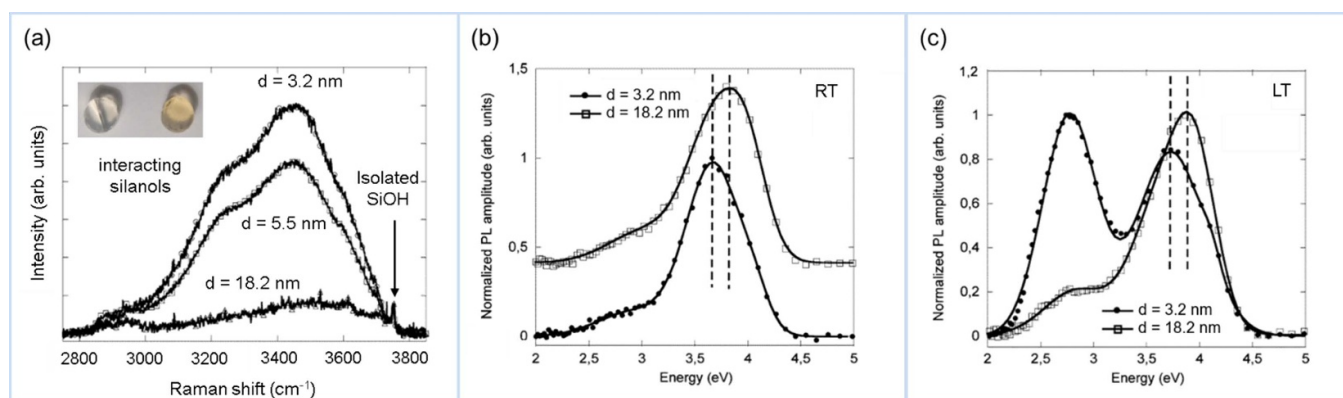


Figure 6. (a) Raman spectra of MS samples with different pore sizes. Reprinted with permission from [31]. Copyright (2003) American Chemical Society. (b) Room temperature and (c) 8 K normalized PL spectra of MS samples excited in the UV. Reprinted with permission from [49]. Copyright (2005) American Chemical Society.

that MS, when excited in the UV, presents three main emission bands, one in the blue, ascribed to self-trapped free excitons, one in the green, assigned to hydrogen-related species at the pore surface, and a red band related to the presence of non-bridging oxygen hole centers both at the surface of the pores or within the silica skeleton [95]. The proposed assignment of the blue-green band was questioned, and other models were considered, calling for the presence of a twofold-coordinated Si surface center [96] whose formation is related to the dehydroxylation process [97] induced by thermal treatment or light irradiation. Besides external stimulus, also the interaction with the surrounding environment can modify the optical features of MS, leading to a decrease of the optical transmission or the quenching of the emission bands, eventually suggesting applications of raw MS in sensing. From one side pollutants can be adsorbed from the environment leading to no more transparent yellowish samples (figure 6(a)).

The contaminants can be easily removed by wet annealing by soaking the samples in oxygenated water and mild thermal treatment (below 100 °C) [32]. On the other side, the chemical or physical adsorption of oxygen species decreases the overall emission efficiency in the blue, green, and red regions because of the interaction of O₂ molecules with emitting centers [71, 96]. As discussed before, the MS surface, unless specifically functionalized, is hydrophilic and covered with different kinds of silanol groups, both isolated and interacting ones, depending on the pore size and pore curvature (figure 6(a)) [31]. Those silanol groups can participate in the formation of different emitting centers, because of the dehydroxylation reaction between two adjacent silanol groups [97] or withstand thermal treatment up to 700 °C, mainly as isolated ones. For these reasons, the hydrophilic silica surface is prone to absorb water and interact with organic or inorganic species flowing within the pores. Aiming at identifying the emitting centers in MS in a series of papers we studied the emission properties of pure MS before and after aging or the modification induced by the interaction with selected solvents and gasses [49, 72]. We found that, when excited in the UV range, two main surface emission bands are always detected, one in the blue and one in the UV range, the blue relative contribution

being larger at low temperatures (figures 6(b) and (c)). The contribution of the UV band was shown to increase as the pore size increased, whilst the blue band did not have any correlation with the pore size. The analysis of the spectral features of both bands did show a smooth shape with no resolved vibronic contribution, as reported in other research papers [50]. The two bands have been both deconvoluted as due to the superimpositions of two slightly different emitting centers, possibly related to two slightly different environments or geometries at the silica surface. We modeled those emissions according to two dehydroxylation reactions expected at the silica surface proposed by Uchino and co-workers [98, 99] and involving adjacent geminal silanol groups. Those reactions lead to the formation of two different surface defect pairs: two facing silylene defects, to which the UV band is ascribed, and a silylene plus a dioxasilirane pair, responsible for the blue emission. By means of DFT simulations and thermodynamic kinetics to account for the reaction with oxygen we verified that those models could explain the observed optical properties [73, 74]. In addition, by analyzing samples with different pore sizes we rationalized that the emitting centers can be stabilized in slightly different geometries with different optical properties, since the increase of the Si–Si distance in larger pore diameter samples produces a slight blue shift of the emissions. However, the assignment was recently questioned [51], reporting some spectra with vibrational features upon the emission whose contribution was increased by annealing in O₂ or H₂ at quite high temperatures. Since MS can contain residual carbon species due to the surfactant exploited during the synthesis or even due to the adsorption of CO₂ from the atmosphere, the formation of some PAHs was considered by the authors. Indeed, the spectra of some PAHs recall the one of the MS, with the typical vibronic features of organic molecules and the emission spectra can be tuned from the UV to the visible range by increasing the number of benzene rings. In addition, the formation of some organic compounds on the silica surface with smooth PL spectra was also reported by investigating the thermolysis of phenyl groups in MS, calling for some possible connection with spectral features of carbon dots (CDs) [100]. However, some open issues concerning the assignment of the

UV and blue emissions in MS remain, since, for example, the formation of PAHs requires a quite high temperature (typically above 650 °C) usually not achieved in the sol-gel synthesis process. Besides, the fingerprinting vibronic features were not always recorded in the spectral analysis of MS optical features. Another open issue regards the interaction with the silica surface eventually involved, through silanol groups, in bridging the carbon species and how this interaction eventually affects their emission properties.

As discussed at the beginning of the section, the optical properties of MS are interesting *per se* aiming at understanding the relationship among composition, structure, morphology, and the observed features. The reported modifications of the transmittance of the MS monolith because of the interaction with the surrounding environment (aging phenomenon) could be detrimental if one is looking for applications in the field of transparent thermal insulation. On the other hand, the same phenomenon could be exploited to monitor air pollution or for oxygen sensing. Clearly, by modifying the surface with specific chemical moieties the drawback can be circumvented and large transparent monoliths of organically modified MS were proposed as new windows with very high optical transmittance and very low thermal conductivity. The transparent windows, potentially useful for energy-saving building systems, were prepared by drying a sol-gel silica network under ambient conditions from a nonpolar, high-vapor-pressure solvent. Organosilica monoliths have a transmittance larger than 95% and a low thermal conductivity of 0.04 W (mK)^{-1} . The organic surface modification was mandatory to achieve a twofold objective: the large porosity (>50%) required to match the thermal conductivity performances of aerogel with a crack-free strengthened MS transparent window; the preservation of the optical transparency, the latter being controlled by the narrow distribution of nanopores (pore size < 15 nm) [4].

Another interesting application of raw MS is the exploitation of silica nanoparticles for the formation of a hierarchical macro-mesoporous structure, providing tunable PC whose photonic gap depends on the size of the nanoparticles [52]. Monodispersed spherical MS particles of about 15 nm were synthesized via a modified Stober method. The MSN nucleate spherical aggregates in the 250–1500 nm range, leading to a structure with different ranges of porosity, due to the aggregation and the arrangement of the nanoparticles into an opal-like film with cubic fcc packing. The photonic bandgap was tuned from visible to IR region by changing the size of the nanoparticles and eventually filling the different range of porosity with gas or liquid media, such as glycerol, to further tune the photonic crystal features. Very recently MS-based PC (m-SiO₂-PC) have found applications as colorimetric concentration detection materials for non-volatile substances. MS particles were prepared starting from dense SiO₂ NPs (figure 7(a)) and growing a mesoporous shell upon them (figure 7(b)). The film of dense and MS particles was obtained by packing the NPs on ordered fcc structures. The refractive index and the reflection peak of the obtained PC can be tuned by changing the NP size (figure 7(c)), displaying color changes because of the adsorption of the detected solution at the mesopore level [53].

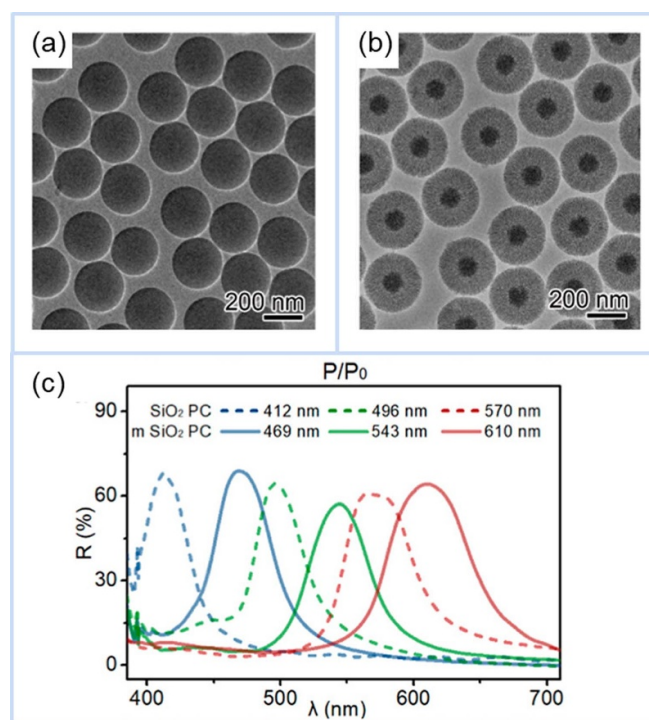


Figure 7. TEM images of (a) SiO₂ (230 nm) and (b) m-SiO₂ (258 nm) particles. (c) Reflectance spectra of SiO₂ and m-SiO₂ PC of different sizes. Reprinted with permission from [53]. Copyright (2023) American Chemical Society.

3.5. Filling the void for photonic and thermoelectric applications

The idea of filling MS with fluorescent molecules was also pursued for photonics applications, for example as solid-state media for lasing, or as emitting media for lightning, since a solid matrix offers a larger mechanical and thermal stability, which are advisable features for these applications. Besides the advantage of being solid systems, so that avoiding the use of hazardous solvents and direct contact with the molecules which sometimes are toxic by themselves, the exploitation of a porous matrix allows, in principle, to increase the dye concentration well above the emission quenching threshold typically observed in solution. Indeed, the silica surface allows anchoring of the molecules in large amounts, and the formation of fluorescent aggregates is usually not observed in solution. The system model typically considers the introduction of a few well-characterized and highly efficient dye molecules, like Rhodamine 6G or B for the xanthene family or 7-hydroxycoumarin for the coumarin ensemble. Among the possible matrices, embedding dye molecules into MS by means of sol-gel versatility can offer the highest physical and chemical performances [33–35]. Basically, there are three ways to introduce specific molecules within the MS host: (1) post-synthesis imbibition, (2) mixing at the molecular level at the sol stage of the synthesis, (3) grafting to the silica surface by using specific silicate precursors with covalently bonded dye molecules. In the first two cases dye molecules are bonded to the silica surface by means of electrostatic interaction (type

I hybrids); in the third case, the dye molecules are bonded to the silica surface by means of covalent bonds (type II hybrids). Clearly, the easiest approach is to introduce the dye molecules by impregnation of the mesoporous matrix, but it suffers from leaching of the molecules by interaction with the liquid environment [36]. On the other hand, since sol-gel synthesis does not imply achieving high temperatures, dye molecules can be mixed at the sol state with no concern for thermal degradation. This allows the production of type I organic-inorganic hybrids where the bonding between dye molecules and silica matrix is non-covalent, thus partially but not completely reducing the leaching drawback, largely relevant in the case of post-synthesis imbibition [37–39]. The best solution is to covalently bond the fluorescent molecules to the silica surface by a proper grafting technique which means the employment of selected precursors during the sol-gel synthesis [40–43]. Another possible solution to solve the leaching phenomenon of type I hybrids is sealing the external surface with a further silica shell or by capping the pores with suitable functional molecules, eventually providing a stimulus-responsive shield (see section 3.6). Beside leaching, aiming at achieving super luminescent systems, the main challenge is the loading limit, since large concentrations of dye molecules can produce aggregation phenomena that can largely affect the electrical and optical properties of the molecules themselves. Indeed, at large concentrations quenching of emission features could reduce the efficiency of these materials, and some strategies to separate molecules by means of *ad hoc* functional splitters have been reported (*vide infra*). The formation of aggregates is related to the large concentration of dye molecules within the MS matrix. Depending on the geometrical configuration different aggregates with different optical properties can be formed. As compared to the liquid media, the presence of the silica surface can drive the formation of aggregates whose geometry depends on the interaction of the dye molecules with the silica surface itself. Among the aggregates, J dimers are fluorescent and display a coplanar sandwich configuration or an oblique head-to-tail configuration. The technological challenge is to control the interaction of dye molecules with the silica surface to control the formation of aggregates, selecting the J ones and increasing the concentration up to the quenching threshold aiming at producing emitting optical devices with very high efficiency or potential media for solid state laser application.

In their pioneering and extensive work on the interaction of model laser dye with MS surface [54, 55], Del Monte and co-workers demonstrated that silica surface allows the formation of fluorescent aggregates far beyond the concentration threshold typically reported in solutions. Indeed, the porous surface acts as an external potential that imposes a driving bias on the concentration-dependent formation of molecular aggregates. The kind of aggregates depends on the chemical and physical features of both the host surface and the guest molecules, both fluorescent coplanar and oblique J-dimers can be formed. As the concentration increases the non-fluorescent H-dimers are also formed, leading to a decrease of the emission features of the hybrids. A detailed analysis of the spectroscopic features of the hybrid systems, by combining optical

absorption, excitation spectra, and emission bands, paired with the decay times of the recorded emission as a function of the dye concentration, allows the identification of the different kinds of aggregates. It was reported that in-plane oblique angle J dimers were formed in the case of Rhodamine 19 [56], Rhodamine B [55], Rhodamine 6G, and Rhodamine 110 [54], whilst coplanar inclined orientation was adopted for Rhodamine 101 and sulphorhodamine B [37, 39]. In the case of Nile Red [57] and Rhodamine B [58] by proper functionalization of the silica surface with organic moieties (GPTMS, glycidoxypolytrimethoxysilane) the aggregation of dye as a function of dye concentration was carefully controlled from planar monomer to oblique J-dimers and finally to nanoparticles formed by means of supramolecular architecture. Those dye nanoparticles overpassed the quenching effect due to concentration thanks to the interaction with organosilica and displayed very highly efficient fluorescence, hundreds of times larger than the emission of single molecules within the same host. Very large concentrations of azo-dye molecules covalently bound to the silica glass backbone were also successfully prepared to obtain efficient nonlinear optical properties leading to photorefractive materials with high optical gain [59].

Besides the formation of aggregates, hybrid systems made of grafted Rhodamine 6G on MS host also showed a larger resilience to photobleaching, a critical issue concerning LED or solid-state laser applications [60]. The formation of J dimers and the interaction with the matrix led to a bi-molecular photobleaching trend as a function of excitation laser pulses because of different environments sensed by the emitting centers in terms of energy release to the matrix and interaction with quenchers (like O₂). In addition, by changing the preparation method or through post-synthesis treatments, like thermal treatments or interaction with selected solvents [61, 62], it is possible to tune the different emitting species for specific purposes. In the case of heavily doped Rhodamine 6G hybrid systems obtained by impregnation, thanks to the larger mobility of dye molecules bound to silica by H-bond in type I hybrids, we were able to promote the modification of fluorescent dimers into monomers upon ultrafast UV laser irradiation. Since the induced transition is thermally reverted, one could develop an optical/thermal memory to check, for example, thermal abuse on drugs or foods [63].

Another possible application in the photonic field regards the hybrid systems with MS and CDs, a new class of carbon-based emitting nanomaterials whose optical features, low toxicity, and green chemistry production attracted a lot of interest. The research on CDs started almost 20 yr ago, boosted by the optical efficiency as emitters in the blue and green region as high as the one of the quantum dots but with no concern for the potential hazard for their application, paired with chemical inertness and biocompatibility. In addition, CDs displayed an unusual optical feature, at least the ones prepared by the bottom-up approach, that is the possibility to tune the emission across the visible range by changing the excitation energy, thus providing multicolor nano-emitters for applications in different technological fields [101]. Up to now, the main open question is related to the relationship between

the structure/morphology of the nanoparticles and their emitting centers [102]. Another open issue is their exploitation at the solid state since the reported efficient optical features are usually observed by dispersing the CDs in solution [103]. However, the interaction with MS was shown to be beneficial for these benign nanomaterials, both regarding their synthesis [104] or the tuning of their optical properties for photonics [64], sensing [105], bioimaging [106], disease detection [107], and cancer therapy [106]. As for the photonics applications, by changing the acid reacting with *o*-phenylenediamine (oPD) in an ethanol-based solvothermal synthesis a palette of CDs emitting at different emission wavelengths across the visible range was obtained and exploited to prepare a white light emitting diode prototype by properly mixing those CDs into a silica sol-gel [64]. Indeed, CDs can be easily integrated into sol-gel protocols because of their dispersibility into polar solvents without modifying the textural properties of the porous matrix. Interestingly, as for the case of dyes, MS was not only exploited as a matrix but also played an active role in selecting and tuning specific features of CDs.

Applications as LED or in the field of anti-counterfeiting were also proposed for N-doped CDs directly synthesized within MS by adding tetramethylammonium hydroxide (TMAOH) to the typical sol-gel synthesis of silica with TEOS [80]. TMAOH first acted as a basic catalyst to drive the formation of silica doped with TMA⁺ ions, then was involved in the pyrolysis of the nanoparticles to get N-CDs embedded within MS (figure 8(a)). These hybrids displayed an efficient excitation-dependent emission both in solution and in the solid state, with tunability from blue to yellow color. Similarly, we modified the surface of N-CDs by using an organosilane, 3-(aminopropyl)triethoxysilane (APTES), allowing to increase the efficiency of their emission and reducing the typical concentration quenching (figure 8(b)). APTES was exploited to achieve both the formation of a silica shell on CD nanoparticles when performing the synthesis in water or to produce CD-doped silica films with emission in the blue and green range [66].

The interaction of silica with CDs was exploited to understand the mechanism of excitation dependence of the emission as well as the origin of the emitting centers of CDs. We analyzed the optical properties of CDs in different kinds of sol-gel silica, namely xerogel, cryogel, and aerogel, showing that of the two main emissions, a blue and a green one, the larger the pore size of the silica host matrix the smaller the relative contribution of the green band of CDs [67]. Accordingly, when MS nanoparticles are impregnated with a water dispersion of CDs, we observed that the relative contribution of the green band was increased, but the overall efficiency of the system was reduced as compared to the quantum yield of the same CDs in water [69]. It was also reported that in the case of CDs confined in a silica network, the excitation-dependence of CD emission is inhibited, being further recovered by the removal of silica [65]. Again, once the CDs were dispersed in water, the blue band was also recovered, supporting the idea that the silica matrix allows tuning the size of the CDs and their composition. Indeed, by synthesizing the N-doped CDs within silica nano-reactors, we were able to elucidate the presence

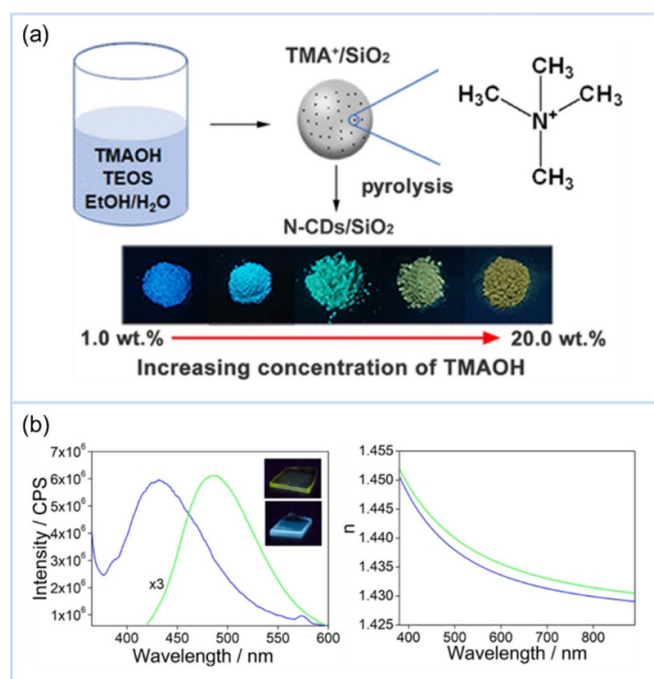


Figure 8. (a) Schematic picture of the synthetic process of N-CD-embedded SiO₂ particles with tunable emission color depending on the amounts of TMAOH used in the reactions. Reprinted with permission from [65]. Copyright (2021) American Chemical Society. (b) Emission spectra and refractive index of APTES-based hybrid sol-gel films containing CDs with different optical properties. Reproduced from [66]. CC BY 4.0.

of both molecular and surface-emitting centers in CDs, the former being more efficient in water solution, the latter being responsible for the emission at the solid state once the molecular centers are quenched because of the concentration effect [68]. Finally, the size and composition of the CDs were tuned by the interaction with the host matrix, allowing to promote the formation of green-emitting N-related molecular centers, thus showing an active role of MS in tuning the structure and properties of CDs (figure 9).

The integration into MS dates to about 10 yr ago. There are no reports, to our knowledge, on the longevity of these systems, the proposed applications being in general on the laboratory scale. In our experience, the optical properties of hybrid samples have been stable over the years by keeping the samples under standard environmental conditions. There are a few reports on the effects of high-power UV irradiation on CDs in solution showing that the irradiation could modify their optical properties, because of photobleaching of the molecular emitting centers, the effect being largely dependent on the kind of samples. In our work on hybrid systems, we observed that MS is involved in the UV induced modification because of the interaction between the emitting centres and the silica surface, promoting the red shift of the optical features till a saturation level. We must underline, however, that this effect is related to high-energy irradiation which should not be expected under normal operation condition of CD/MS devices.

Concerning the applications in the thermoelectric field, it was proposed that MS matrices could be exploited to increase

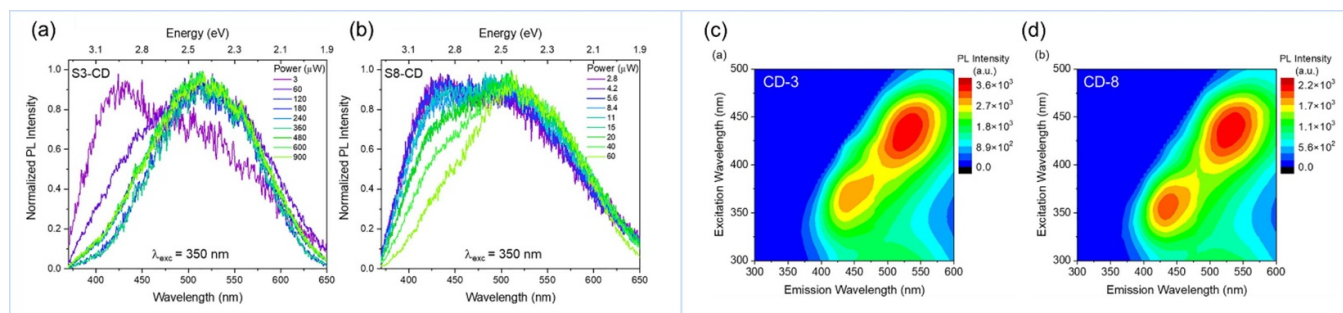


Figure 9. (a), (b) Normalized emission spectra of two MS-CDs systems as a function of fs UV laser irradiation. (c), (d) Excitation/emission maps of CDs synthesized within MS of different pore size (3 and 8 nm) after extraction from the silica matrix. Reprinted from [68], Copyright (2023), with permission from Elsevier.

the figure-of-merit (ZT) of thermoelectric materials to values larger than one. Indeed, nanostructured materials could in theory have a 10-fold increase of the thermoelectric features because of their size effects, provided that their diameter is lower than the typical thermal de Broglie wavelength (less than 10 nm) [75]. One can use microporous and mesoporous materials as a template to grow nanometric thermoelectric materials with proper diameter and orientation, to increase the electric conductivity and decrease the thermal one of the composites. The addition of MS to Nb-doped SrTiO₃ bulk materials [76] was shown to reduce the thermal conductivity and enhance the electrical conductivity significantly with no effects on the Seebeck coefficient, thus increasing the overall figure of merit. In this case, the effect was mainly due to the MS-driven formation of Sr₂TiSi₂O₈ crystals mainly distributed in the grain boundaries of the Nb-SrTiO₃ composite. Silica nanoparticles were also applied in the synthesis of silica/carbon thermoelectric nanocomposites where the presence of the silica allows for the reduction of the thermal conductivity of the system, thus increasing its ZT [77]. Recently, we also investigated the possibility of exploitation of MS to increase the thermoelectric features of PEDOT (Poly(3,4-ethylenedioxythiophene)), probably the up-to-now best thermoelectric material working at low temperatures [78]. Besides the thermoelectric field, hybrid materials made of PEDOT and MS have been recently proposed as promising systems for electrochromic devices [108] and capacitive humidity sensors [109]. PEDOT is an organic polymeric chain with high electric conductivity and very low thermal conductivity whose electric conductivity is usually increased by doping with PSS (polystyrene sulfonate) to provide further charge carriers. However, the doping procedure also increases the thermal conductivity, thus not providing the expected results on the ZT. Another solution is to find a way to synthesize longer and aligned polymeric chains, achieved by a change in the configuration of the chain itself, from a coil configuration (benzoid structure) to a linear one (quinoid structure). Following this idea, we performed the synthesis of PEDOT by chemical oxidative polymerization within the SBA-15 MS template [78]. As compared to secondary doping usually considered to promote the PEDOT conformational change, we were able to show, by Raman and XRD measurements supported with computational chemistry calculations, that the confined polymerization of PEDOT into

MS also causes a similar conformational change, the templated synthesis favoring the formation of longer and with larger molecular weight polymer chains.

The reported examples refer to two different interactions of MS with thermoelectric materials. In the first case, the ordered mesoporous matrix is selected as a template to produce nanowires of the materials with selected dimensions. In the second case, MS nanoparticles are mixed with the thermoelectric material aiming at reducing the thermal conductivity of the composite. The templated synthesis effectively produces nanowires with nanosized diameter and larger crystallinity but does not reach, at the moment, the expected improvement in the thermoelectric features. Indeed, if the MS matrix is kept obtaining a device with aligned nanostructures, the thermal conduction of the matrix does not allow to improve the figure of merit of the hybrid system as compared to the one of the bulk materials. On the other hand, if the MS is removed, the obtained nanowires are difficult to disperse after extraction to prepare a conductive film. Thus, the challenges for the templating approach are to reduce the thermal conductivity of the template or to increase the dispersibility of the synthesized materials. In the second approach, the figure of merit is increased by reducing the overall thermal conductivity and increasing the electrical conductivity. This is obtained thanks to the thermal properties of the thermoelectric material grown at the interface with MS nanoparticles (in the case of MS/C system) or at the grain boundaries of the composite (in the case of MS/Nb-SrTiO₃ system), the growth of the grains being affected by the presence of MS. This approach appears more promising in terms of scalability to the market because the composites can be obtained by both standard sintering procedures or new methods, like ball-milling or sonication [110, 111]

3.6. Applications in the biomedical field

One of the most fascinating fields of applications of MS is the biomedical one, for both bioimaging and drug delivery [29, 112, 113]. The working concept of a drug delivery nanosystem is a hybrid composite where the loaded MSN is shielded with a proper envelop layer in order to travel within the biological fluids with no leaching of the carried drug. The sealing layer also allows the passing of the bio-barriers by means of proper functionalization and delivers the drug to the

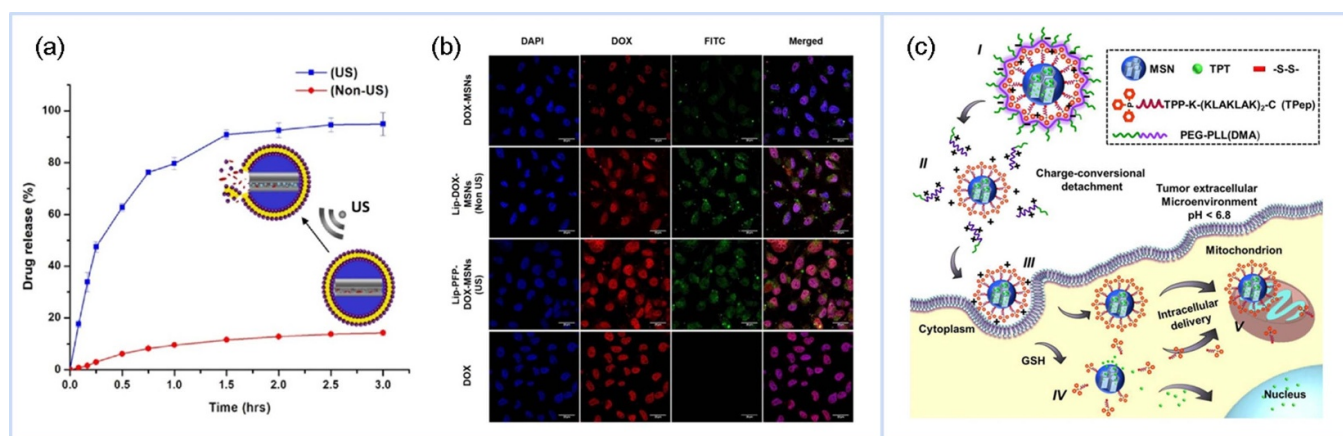


Figure 10. (a) *In vitro* drug release of DOX under US stimulus from two DOX-MSN systems. (b) Confocal microscopy images of cellular uptake with FITC-labelled NPs, showing localization of DOX in the nuclei. Reproduced from [114]. CC BY 4.0. (c) Operation scheme of a pH-sensitive MNS-TPT-TPep nanosystem. Reproduced from [115], with permission from Springer Nature.

required target. The delivery can be both externally or internally stimulated, for example by pH, enzyme, redox reaction (internal stimulus) or by light, temperature, magnetic field, or ultrasound waves (external stimulus). In figure 10(a) it is reported an example of stimulus-responsive drug release from MS nanoparticles upon irradiation by ultrasonic (US) waves [14]. The *in vitro* release profile of two different systems composed of lipid-coated MSNs is reported for a time period of 3 h. Doxorubicin (DOX) is the anticancer drug encapsulated with or without perfluoropentane (PFP) inside the MSN pores. PFP is a US-responsive agent upon US irradiation. The lipid layer also improved the cellular uptake, acting as a gatekeeper at the pores further removed by US stimulus after uptaking to trigger the drug release. Almost 100% release is obtained in 3 h. In figure 10(b) the confocal images show the localization of DOX (red) in the nuclei, stained with 4',6-diamidino-2-phenylindole (blue). Similarly, pH-responsive multifunctional MSN-based enveloped nanosystem can perform a double delivery to tumor cells, releasing both the antineoplastic drug, topotecan (TPT), and therapeutic peptide (TPep) to destroy both the nucleus and tumor mitochondria. The operation of the pH-responsive multifunctional MSN-based enveloped nanosystem is reported in figure 10(c). The presence of PEG-poly(L-lysine) (PLL) and 2,3-dimethylmaleic anhydride (DMA) moieties makes the nanocargo sensitive to the acidic pH of the tumoral extracellular microenvironment, allowing cellular uptake and release of TPT and TPep to tumor cells. MS-based hybrid systems responsive to pH or infrared light external stimuli were also reported as carriers in the treatment of specific pathologies, like osteoporosis [79], or to kill bacteria under 800 nm laser irradiation in a double photothermal and drug-releasing antibacterial activity [81].

We worked on a multifunctional hybrid system for drug delivery and fluorescence imaging, made by PEG-supported hydroxyl coumarin introduced within MS nanoparticles [82]. Coumarin is a drug exploited as anti-tumoral or anti-HIV and also possesses well-known emission properties in the blue region. However, coumarin is poorly soluble in water, and for this reason, we supported it by PEG hydrophilic polymers.

Release of the drug under a simulated biological environment was proved by detecting the blue emission band after removal of the NPS, thus allowing, in principle, the exploitation of both therapeutic and imaging features of the coumarin. Finally, a specific sealing approach can be considered not only to trigger the drug release at the selected target but also to increase the efficiency of the bioimaging. We proposed a method to seal the pore surface by exploiting the presence of the surfactants applied to synthesize the MS nanoparticles [83]. In addition, the template system, CTAB in our case, also separated the dye molecules within the pores, reducing aggregation and increasing both the loading threshold and emission efficiency. The Rhodamine 6G doped MS composite that was prepared had superior sealing features due to a final low porous silica shell surrounding the NPs. We were successful in controlling the aggregation of the dye within the nanosystem, reaching a high quantum yield of the emission. Indeed, the brightness of the fluorescent hybrids, as compared to other similar systems, was very high, up to 100 times larger than the brightness of CdSe/ZnS quantum dots. In addition, these nano-cargos displayed very good ability to stain the nucleus of the cells, as compared to the dye alone, and high photostability, allowing very good seconds enduring imaging results (figure 11).

Drug delivery systems require 'zero release' of the cargo before reaching the targeted sites. Although slow-down release can be obtained by adjusting the length, size, and interconnection of the pores, a real smart and controlled delivery can be achieved by gated systems, where the gates of the pores are opened by specific stimuli like pH, temperature, enzyme, redox, light, magnetic field and so forth. Gating is obtained by surface modification of MSNs and should also not hamper or improve dispersibility and *in vivo* circulation time, pivotal issues to realize efficient drug delivery systems. For example, PEG and lipids can provide larger solubility and biocompatibility, surfactants can act as chemosensitizers or pore sealers. Clearly, all the chemical solutions used to functionalize the pores should be biocompatible and should prevent aggregation of nanoparticles. Most of the studies on stimuli-responsive release focused on *in vitro* applications but there are

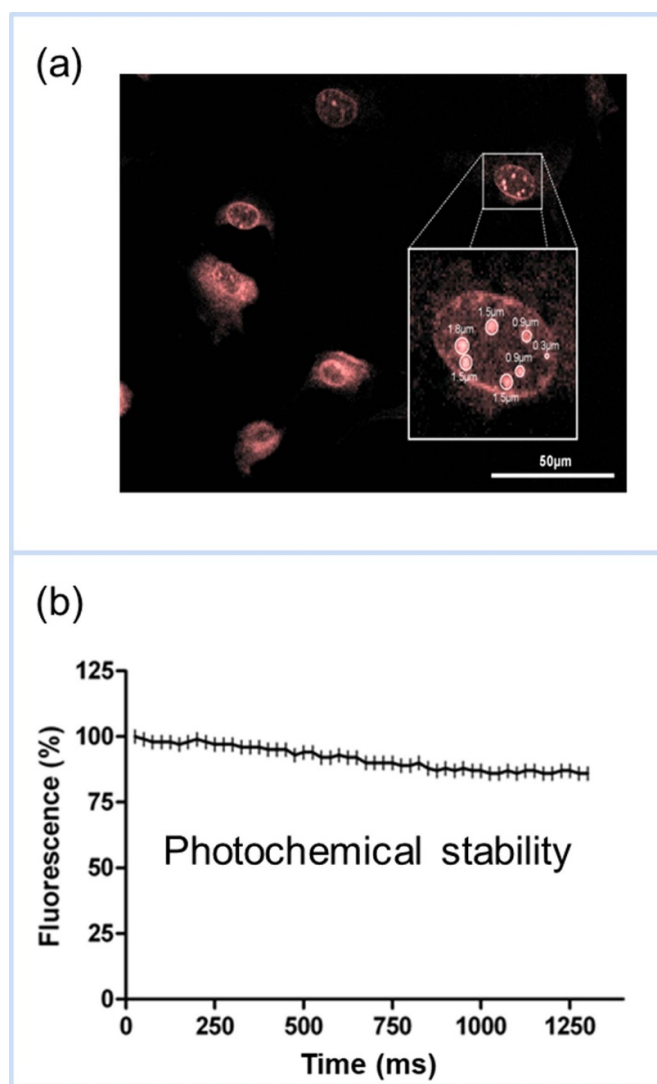


Figure 11. (a) Confocal image of stained cells with Rh6G-MS hybrids and (b) photochemical stability of the hybrids. Reprinted from [83]. Copyright (2016) with permission from Elsevier.

indications that pH and enzyme-responsive gates are efficient *in vivo* experiments on animals [15, 116]. Since the extracellular pH of tumor tissue is significantly lower than healthy tissue pH and there exist specific tumor-related enzymes and chemicals, MSN drug delivery systems based on pH and enzyme stimuli are promising for cancer treatment. It was also proved to be an efficient alternative in treating pH-sensitive bacterial infections. In addition, multi-modal systems exploiting magnetic functionalization for targeting and monitoring paired with IR light-responsive gates were successfully applied on *in vivo* experiments to treat tumors in nude mice. Other stimuli like ultrasound, magnetic or electric fields appear at the moment more challenging for applications *in vivo* although promising results *in vitro*, in particular for ultrasound stimulus, suggest the possible use of the latter to control the release of the drug to the target sites.

Besides bioimaging and drug delivery, another relevant application of MS in the biomedical field is biosensing. By

doping MSN with aptamers high sensitive biosensors for various bioanalyte can be prepared [84]. In most cases, by modifying the aptamers or loading in the MS matrix-specific dyes the sensed analyte is measured by detecting the emitted light. In the context of biosensors, MS found also a large application in glucose sensing. The MS features were exploited in different ways, from one side as a non-toxic biocompatible coater to protect glucose sensors [85]. On the other side, MS was an active element in an electrochemical biosensing platform where a layer of MS host phenylboronic acid molecules that could react with glucose, providing sensitive enzyme-free sensors [86].

Biocompatibility and toxicity are relevant issues concerning the application of any kind of nanomaterials to the biomedical field. Despite silica is in general regarded as biocompatible and atoxic, there is not a consensus on the potential effects of MS nanomaterial exploited for drug delivery and bioimaging. The focus is in general on the therapeutic effects rather than on biosafety and the lack of a validated large dataset hamper the transition to human clinical trials. However, it was reported in an *in vivo* experiment on mice that the MSN tends to accumulate in the liver and spleen, in particular by means of intravenous administration [14]. In the biological environment, silica can be degraded in silicic acid further excreted through kidneys, thus providing biodegradation. Of course, increasing the latter by means of proper MS functionalization [117] is one of the most relevant challenges in biomedical applications. Indeed, silicic acid is cytotoxic in high concentrations thus a fast removal is required paired with a dose evaluation. To further boost the application *in vivo* and foster the transition to human experiments the characterization in physiological conditions of the administrated MS devices by means of novel non-invasive techniques able to follow the outcomes of the carriers and the delivered drugs are mandatory [118].

4. Conclusions and perspectives

In conclusion, the survey presented here clearly demonstrates that silica is an endlessly versatile material whose horizons were further expanded by the discovery and potential industrialization of MS. High specific surface area, large pore volume, tunable nanosize, high biocompatibility, and easiness of surface functionalization are unique features of MS for technological applications. As a consequence, mechanical, electrical, thermal, and optical properties of void MS have been exploited for thermal insulation, particle and spilled oil loading, catalysis, photonic crystal design, and oxygen or pollution detection. Moreover, thanks to its nanosized morphology and texture, MS can be exploited by filling its void space, thus allowing the engineering of specific composites with applications in photonics, sensing, thermoelectric fields, or biomedicine for bioimaging, drug delivery, and biosensing. However, several challenges must be addressed before these composites can be brought to the market. For instance, there is a need for synthetic routes that can be easily and advantageously transferred to the industry, potentially using industrial

waste such as rice husk ash or the vast amounts of oil shale ash worldwide, containing up to 60% of silica [6]. Recent advances in computational modeling of silica self-assembly and condensation reactions now enable us to predict the final structure of porous silica materials. This paves the way for synthesizing MS under environmentally friendly conditions and in a more economical approach [119]. Scaling up the production of MS host and composites to a commercial scale for practical applications is challenging in terms of synthesis yield and material collection, uniformity, and reproducibility of MS material. Aiming at mass production of MS new sources and new processes must be conceived, looking for biodegradable templates or template-free methods to synthesize MS. It is also necessary to reduce the number of synthetic steps, to decrease the time production, and reduce the amount of hazardous waste, carrying out synthesis under safe conditions [14].

The preparation of standardized MS at the production scale is another relevant issue to foster the transition to the market. Among the applications the ones in photonics and biomedical fields require a high level of uniformity and reproducibility with minimal batch-to-batch variation, to grant biosafety and efficiency. Stability is also an issue for catalysis at high temperatures (>500 °C) or in alkaline environment [29]. Recyclability and long-term efficiency, eventually under harsh conditions like high temperatures or under UV irradiation, must also be addressed for all the applications proposed for MS and MS composites. Among them, the larger concerns are towards the biomedical field, foreseeing translation from animal to human clinical trials. As reported, most of the research dealt with *in vitro* experiments and only a few studies regarded *in vivo* tests on mice. Despite some controversial results, which could be due to different preparations and treatments of nanoparticles, there is a general expectation that MS could be engineered to accomplish full biocompatibility. The main aspects to be considered before clinical translation can be accomplished are dispersibility, degradation, chronic exposure effects, and long-term toxicity. Various animal models should also be taken into account as different administration routes, typically implying different functionalization of MS surface [15, 16, 120]. Up to now, only solid silica nanoparticles with no or small pores have been clinically evaluated, but recently FDA approved the investigation of fluorescent core-shell SiNPs [121] for diagnostic purposes in cancer, promoting the research on MS safety.

Finally, it is mandatory to understanding the chemical and physical properties of the matrix to explain and fine-tune the interaction with fillers at the atomistic scale for the selected applications of the nanosystems. To achieve this goal, both the extensive experience with bulk silica and the development of complex multi-scale, multi-component, reactive assembly systems are essential. These systems can model the inter- and intra-molecular interactions during the assembly of the composites, allowing engineering the manufacturing of these promising nanomaterials for our future.

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