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Abstract

This chapter describes nanocomposites where at least one of the phases has been obtained by the sol-gel method. In the first part, the synthesis of the nanocomposites is considered, and an attempt is made to resume the general principles and methods related to different classes of materials, with oxide, hybrid organic–inorganic, and polymeric matrices and oxide, metal, and non-oxide nanoparticles. The second part is devoted to the applications of sol-gel nanocomposites. Representative examples of nanocomposites that potentially can have commercial application are described, based on the literature of the last 10 years.

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Introduction

The development of sol-gel nanocomposite materials has been mainly driven by their potential use in many applications, and commercial sol-gel nanocomposites are already part of manufacturing technology.

IUPAC defines a nanocomposite as a “composite in which at least one of the phases has at least one dimension of the order of nanometers,” where “composite” is a “multicomponent material comprising different (nongaseous) phase domains in which at least one type of phase domain is a continuous phase.” We may define sol-gel nanocomposites as those in which at least one phase is obtained by the sol-gel method. Often, in the literature, homogeneous monophasic hybrid sol-gel materials are named nanocomposites, in clear contradiction with the above definition. Of course, borderline situations exist, where the distinction might be a matter of discussion, but these will not be considered here.

The matrix (continuous phase) material, usually classifies composites, allowing to distinguish among metal, ceramic, polymer matrix. In the case of sol-gel nanocomposites, metal matrix is excluded, but a further type of matrix, the hybrid organic–inorganic one, is added.

As for usual composites, the combination of different materials allows to obtain a new material with new and tailored properties (mechanical, thermal, electrical, or optical).

The most important difference between a traditional composite and a nanocomposite is the area of the interface between the matrix and the dispersed phase. In nanocomposites, this is much larger, and very often this allows to obtain huge effects even with small amount of the second phase. Furthermore, the specific properties of the nanophase are introduced.

The application of the sol-gel method to the synthesis of nanocomposite materials started to emerge in the literature approximately at the end of the 1980s. Since then the number of published papers increased continuously. Looking at the number of published papers, as reported by the Web of Knowledge using the keywords “sol-gel” and “nanocomposites,” it comes out that from the beginning of the millennium the growth has been linear, arriving at more than 500 in 2015.

Initially the idea to start from a single batch was very attractive, and the first efforts were addressed to the so-called “in situ” strategies. The development of hybrid organic–inorganic materials was almost contemporary and gave an important contribution to the control of the matrix-dispersed phase interface. Then “ex situ” methods started to attract the interest of researchers because of the possibility to better control the final microstructure of the nanocomposite.

Among the most interesting features of the sol-gel approach to nanocomposites is the possibility to get them as thin films to coat every type of substrates, and many applications deal indeed with high-tech coatings and varnishes.

Synthesis of Sol-Gel Nanocomposites

The synthesis of nanocomposites is successful if one succeeds to get a homogeneous dispersion of nanometer size particles, constituting the dispersed phase, in the matrix, avoiding aggregation and particle growth phenomena. This is not simple at all. Aggregation phenomena are driven by the tendency of the system to reduce the interface energy, which is very high in the case of nanoparticles. When the nanocomposite is obtained from a single batch where nanoparticles are dispersed in the sol which will originate the matrix, the dispersions may be stabilized electrochemically (thermodynamic approach) by increasing the electric double layer thickness or through steric stabilization (kinetic approach) by decorating the surface with surfactants. However, aggregation may occur also in the already-synthesized nanocomposite. The stability of the nanostructure with time and temperature depends on the tendency, and possibility, of the nanoparticles to aggregate. There are two different strategies to try to solve this problem: modifying the surface of the nanoparticles to reduce the interface energy or reducing the mobility of the particles, for example, by linking them to the matrix with covalent bonds. This last approach is largely used in the synthesis of sol-gel nanocomposites.

The interface between the matrix and the dispersed phase is important not only for avoiding or limiting aggregation and growth but also for controlling the properties of the nanocomposite material.

Nanoparticles can be functionalized using monofunctional or bifunctional ligands. In the first case, the effect is limited to the modification of the nanoparticle surface, leaving the control of interface reactions to weak interactions with the matrix. Bifunctional ligands are, instead, the way to get a strong interaction with the matrix. The nature of the ligand determines the type of interaction and the effect on specific properties. For example, linking the nanoparticles to the matrix network helps to avoid (or limit) nanoparticle aggregation; using spacer groups between the two reacting groups in the ligand and changing their length and flexibility allow to control the stress transfer between the matrix and the particle, tailoring the mechanical behavior (stress relaxation capability, fracture toughness, elastic moduli, hardness, resilience modulus, etc.).

There are three main general approaches used to modify the surface of nanoparticles: chemical treatments, grafting of polymers, ligand exchange (for a review, see Kango et al. 2013).

Chemical treatments are those where the surface of nanoparticles are modified using moieties, different from the native ones. As an example, both oxides and metals, which surface is usually oxidized, exhibit hydroxyl groups which may react with alkoxy silanes, epoxides, and alkyl or aryl isocyanates.

Inorganic nanoparticles may be “decorated” with polymers by the “grafting” approach. There are two different strategies, “grafting to” and “grafting from,” schematically represented in Fig. 1 (Achilleos and Vamvakaki 2010). The “grafting to” method is based on linking macromolecules onto the surface of the nanoparticle using the affinity of the polymer end group for the functionalities present on the

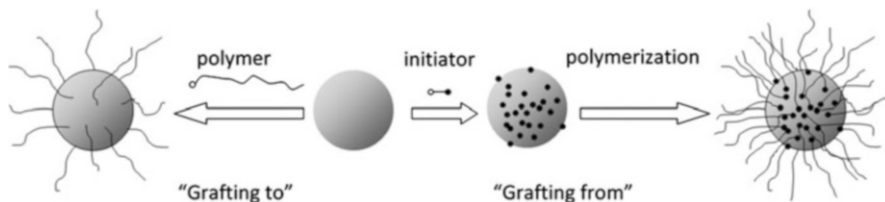


Fig. 1 Schematic representation of the “grafting to” and “grafting from” methods for the decoration of particles with polymers

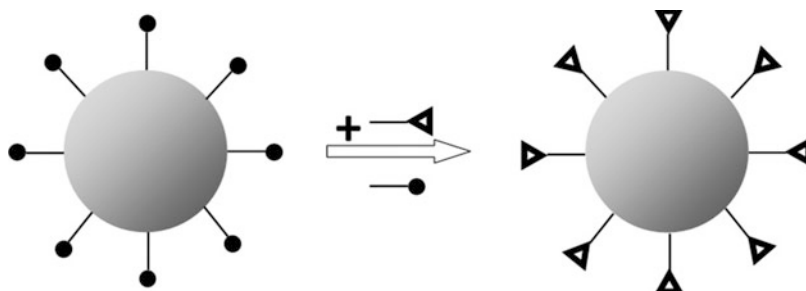


Fig. 2 Schematic representation of the ligand exchange method

particles. The “grafting from” method is, instead, based on the growth of the polymer chains from initiators present or generated on the particle surface. This second approach allows to obtain, in general, a higher density of grafted molecules.

Ligand exchange is a very important reaction for preparing functionalized inorganic nanoparticles. It is based on the substitution of ligands present on the particle surface (outgoing ligands) with ligands present in the surrounding environment (incoming ligands), which link to the surface stronger than the substituted ones (Fig. 2).

This method makes it possible to modify nanoparticles with ligands that cannot be introduced during their synthesis. Although the comprehension of the mechanisms is not complete, the chemistry offers many opportunities, and this is a very important method to design both composition and structure of nanoparticles surfaces (Caragheorghopol and Chechik 2008).

Playing with sol-gel allows to work also on the matrix to optimize the interaction with nanoparticles, by introducing functional groups in the network. The development of hybrid organic–inorganic materials opened many new possibilities in this direction.

“In Situ” and “Ex Situ” Methods

Sol-gel nanocomposites may be obtained following “in situ” or “ex situ” strategies.

In situ methods are based on the preparation of one batch containing the precursors for the matrix and the dispersed phase. Nanoparticles are formed by chemical reaction contemporary to the network development or by thermally induced phase separation in

the already generated matrix (inorganic or hybrid organic–inorganic) in the case of “all sol-gel” nanocomposites or in a polymer matrix through sol-gel reactions.

An advantage of the *in situ* approach is the reduced number of steps in the preparation. A major drawback is given by the possibility of interactions between the processes giving rise to the two (or more) phases, which makes the control in the development of the micro-/nanostructure very difficult or sometimes even impossible.

The *ex situ* methods are based, in general, on the separation of the procedures to get the matrix and the dispersed phases, and the systems are mixed together in a second step. The separation allows to get a much finer control of the final microstructure by avoiding as much as possible any interactions among different chemical processes.

The “*in situ*” approaches for the synthesis of sol-gel matrix nanocomposites take advantage of the potentiality of the sol-gel method to include, in one liquid batch, all the precursors necessary for the development of the matrix and the dispersed phase. In general, the matrix is obtained by the usual hydrolysis and condensation reactions, and the precursors for the dispersed phase remains inside the matrix as precipitated salts or in a dispersed ionic state. In the last case, the phase separation is induced by chemical reactions or by thermal treatment. A general scheme is reported in Fig. 3.

A sol containing the precursors for the matrix and the dispersed phase is prepared starting, generally, from two separate solutions. Both may be, in some way, processed before mixing, but the result of mixing is a one-phase system. Hydrolysis and condensation of the precursors, usually alkoxides, give rise to a gel matrix that may be transformed in a xerogel or an aerogel upon drying. The dispersed phase may be generated in the liquid sol, in the wet gel, or in the dried xerogel or aerogel by means of chemical reaction between metal ions and anions provided by components already present in the original sol or introduced in a later stage. A second way to get the dispersed phase is by thermal treatment of the gel, during the drying process or during densification at higher temperatures.

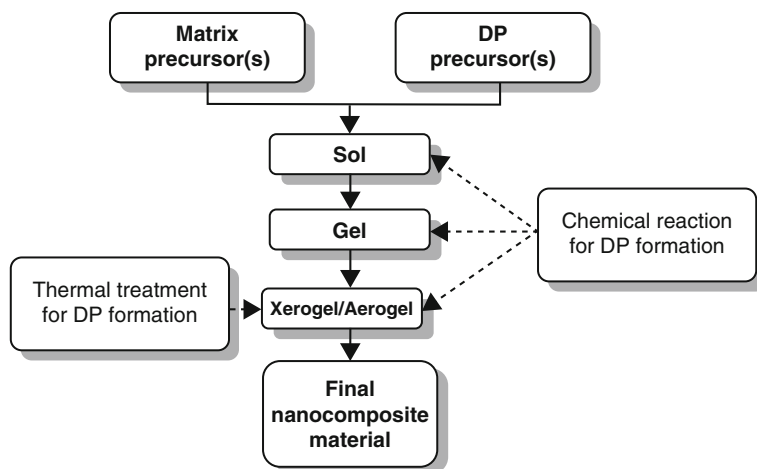


Fig. 3 General scheme of the “*in situ*” synthesis strategy. *DP* dispersed phase

The in situ synthesis has been used mainly to prepare nanocomposites made of an oxide or hybrid organic–inorganic matrix, but there are interesting examples of polymeric matrix nanocomposites with oxide nanoparticles generated “in situ” by the sol-gel method.

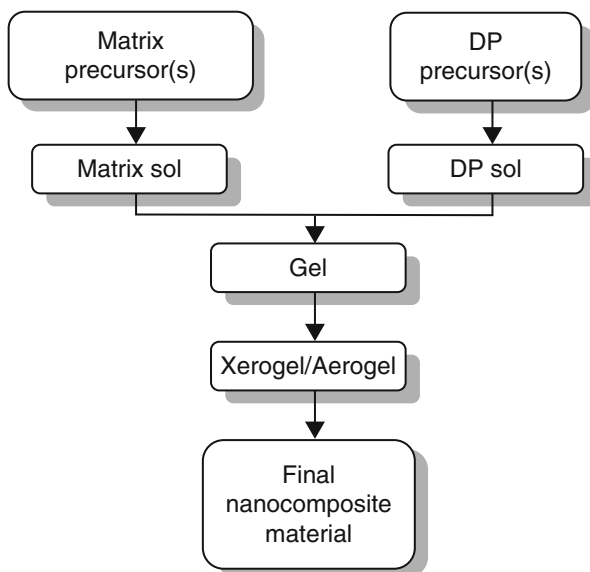
The aim of the “ex situ” approach is to keep the processes for the production of nanoparticles and for the synthesis of the matrix independent as much as possible, in order to reduce the interactions between the two processes. Clearly ex situ processes may be the combination of different synthesis methods. It will be referred to sol-gel nanocomposite if at least one of the phases is obtained through sol-gel reactions. In the case of an “all sol-gel” nanocomposite, the general scheme for the synthesis is the one shown in Fig. 4.

Nanocomposites with Oxide Nanoparticles

In the case of oxide nanoparticles dispersed in a sol-gel inorganic matrix, the chemical affinity is much higher and there is competition between self-aggregation of particles and linking (through weak or strong bonds) of particles to the matrix, which might, in some cases, avoid the agglomeration problem. With hybrid organic–inorganic matrices, the nature of the organic moieties may modulate the affinity, allowing a better control of the interaction.

The results reported in the literature seem to confirm this picture, offering examples of homogeneous nanocomposites obtained in very simple ways, without specific chemical modifications, and examples where a quite complicated chemistry is necessary to get acceptable results.

Fig. 4 General scheme of the “all sol–gel” “ex situ” synthesis strategy. *DP* dispersed phase

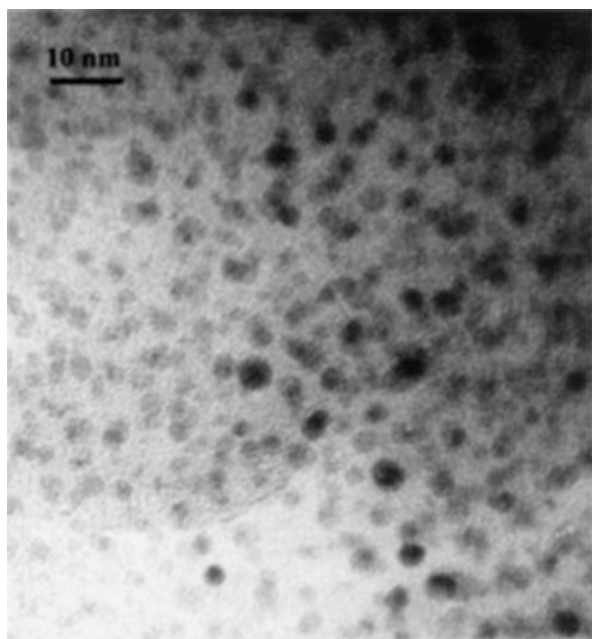


Looking at “in situ” methods, important basic concepts have been published by Breitscheidel et al. (1991) in a paper devoted to the preparation of metal complexes in inorganic matrices. As a first step of the synthesis, the authors obtained a dispersed metal oxide phase by using bifunctional ligands of the type $X - Si(OR)_3$, with $X = NH_2, NHCH_2CH_2NH_2, CN, CH(COMe)_2$, able to form stable complexes with transition metals and, at the same time, to participate to the sol-gel reactions. This approach was the key to get a homogeneous distribution of the metal ions into the gel network. After thermal removal of the organic groups, oxidation of the metal ions took place, giving oxide nanoparticles.

Several examples of the application of this concept may be found in the literature. Our group published several papers, since 2003 (Martucci et al. 2003a), with the goal to fabricate optical gas sensors sensitive to reducing gases (CO, H_2 , etc.). The nanocomposites were based on sensitive oxide nanoparticles, such as NiO, SnO_2 , and Co_3O_4 , finely dispersed in a porous silica matrix. Up to 40% mol metal oxide could be homogeneously distributed in the matrix by using $NH_2(CH_2)_3Si(OR)_3$ (aminopropyltriethoxysilane, APTES) or N-[3-(trimethoxysilyl)propyl]-ethylenediamine (DAEPTMS) as bifunctional ligands and a mixture of TEOS and MTES for the matrix (Martucci et al. 2003b, 2004a, b; Cantalini et al. 2005) (Fig. 5).

The same route was used to obtain more complex nanocomposite films, containing both NiO and Au nanoparticles in silica (Buso et al. 2007a) and in titania (Della Gaspera et al. 2010a) matrices. With “ex situ” methods, the most important aspect for the successful synthesis of homogeneously dispersed nanocomposites is

Fig. 5 TEM image of SiO_2 porous matrix containing 20% mol of NiO nanoparticles (From *J Am Cer Soc, Nanostructured Silicon Oxide–Nickel Oxide Sol-Gel Films with Enhanced Optical Carbon Monoxide Gas Sensitivity*, 86, 2003b, 1638–1640, Martucci A, Pasquale M, Guglielmi M, Post M, Pivin JC, Springer Science+Business Media with permission of Springer)



the surface modification of oxide nanoparticles. Due to hydrogen bonds, the particle-to-particle interaction is very strong, and it is very easy to get irreversible agglomeration when the distance among particles decreases with change of pH or evaporation of the solvent, as clearly discussed by Schmidt et al. (1998). An effective way to keep the interaction under control is the substitution of hydroxyl groups with controllable functional moieties with tailored reactivity as previously discussed.

An example can be found in Peeters (2000) where colloidal silica particles have been incorporated in silica or silica-based hybrid organic–inorganic sol-gel matrices by functionalizing the particles with methyltrimethoxysilane (MeTMS) and using the same molecule as precursor for the matrix. Critical for the success of the synthesis was the size of the oligomers formed by condensation of the hydrolyzed species generated during the pre-hydrolysis step. Large oligomers were found to not react with the silica surface, probably due to their apolarity, while small oligomers could cover the silica particles with approximately a monolayer of MeTMS molecules, with their methyl groups probably oriented toward the outside.

A second interesting example is given by the use of boehmite as nanofiller for hybrid matrices. Commercially available boehmite nanoparticles could be stabilized in a mixture of GPTS and TEOS, by substitution of acetic acid, the initial stabilizer in water, with the silanes (Schmidt et al. 1998). In this case, a further interaction between particles and the matrix was given by the influence of Al-OH groups, behaving as Lewis acid, on the epoxy ring opening and organic polymerization.

Nanocomposites with Metal Nanoparticles

Nanocomposites with metal nanoparticles are of interest because of their optical, electrical, and catalytic properties.

The *in situ* synthesis of this type of nanocomposites follows the general scheme reported in Fig. 6.

All the precursors necessary for the formation of the matrix and the dispersed phase are mixed, and the formation of metal nanoparticles may occur by different reduction processes directly in the sol or in the gel, at different stages of its drying and thermal treatment. Nanocomposites containing a metal oxide as dispersed phase may be transformed by reduction of MO nanoparticles into metal nanoparticles.

Sodium citrate, hydrogen peroxide, citric acid, hydrogen, formaldehyde, etc., may be used as reduction agents, along with polymer stabilizers, such as polyvinyl alcohol and sodium polyacrylate, to control the particle growth. Both the reduction agent and the stabilizer have an important effect on the size and size distribution of particles. Stronger reduction agents favor a fast formation of many nuclei, giving smaller particles. With slow reduction reactions, both wide and narrow size distributions can be obtained, depending on parameters such as the concentration of precursors, pH, temperature (Cao 2004).

Three different approaches have been reported in the literature in early 1990s, putting the basis for further development: (a) reduction of metal oxide to metal

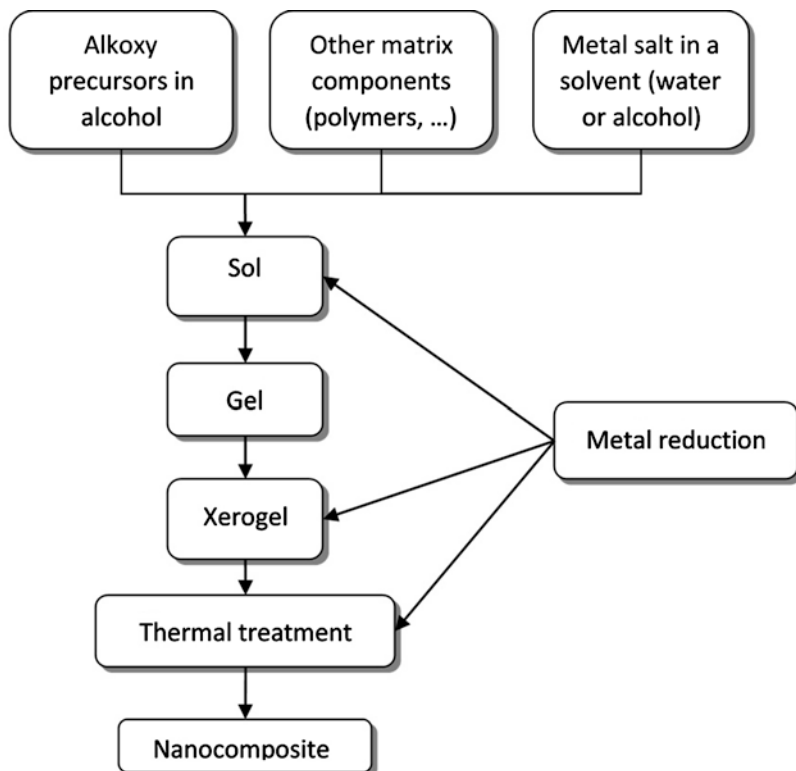


Fig. 6 General scheme for the “in situ” synthesis of nanocomposites based on sol–gel matrices and metal nanoparticles

nanoparticles by thermal treatment under hydrogen (Breitscheidel et al. 1991), (b) treatment of an aged gel with a reducing solution (i.e., formaldehyde to completely reduce silver) (Datta and Das 1992), and (c) reduction of a metal salt in the sol by UV irradiation at room temperature (Mennig et al. 1992).

The important basic ideas in these reports are as follows: the reduction of metal ions may be achieved at different steps of the process; the reduction may be induced by chemical reactions, irradiation, or thermal treatment; and the control of growth and dispersion by linking of metal ions or complexes to the originating matrix network may be obtained by the use of multifunctional silanes, which form complexes with unreduced metal ions at the surface of clusters.

The thermal precipitation in the xerogel at relatively high temperatures is certainly the worst from the point of view of size and size distribution control. Furthermore, metal ions may strongly affect the pore formation process of silica gel during drying and heating (Takahashi et al. 2000).

The generation of particles in the sol is, instead, the most promising approach, especially if the sol-gel process for the matrix formation may be, in some way, taken

separated from the one for NPs growth. This idea is at the base of the “ex situ” methods, but brought to an interesting intermediate approach proposed by Giacoin (Giacoin et al. 1994).

Silver and gold NPs were precipitated at room temperature in the sol containing the metal precursors (AgNO_3 , HAuCl_4) by irradiation with γ -rays. Hydrolysis and condensation reactions of alkoxides were then allowed by slow diffusion of water from a H_2O -saturated outside inert atmosphere. The growth of metal nanoparticles is obtained by colloidal chemistry in the same solution that will give rise to the matrix, but the two steps are sequential in time, allowing a better control of both.

An “ex situ” method to prepare Au-loaded TiO_2 thin films was reported by Della Gaspera et al. (2012). It is based on mixing 5% of gold nanoparticles, synthesized by the Turkevich method, and 95% of titania nanoparticles, obtained by hydrolysis of titanium isopropoxide, followed by thermal sintering. Highly crystalline porous nanocomposite films sensitive to CO were obtained by this way.

Nanocomposites with Chalcogenide or Halide Nanoparticles

Silicate glasses doped with chalcogenides or halides nanocrystals were firstly obtained by the sol-gel method by Nogami in the early 1990s (Nogami et al. 1990a, b, 1991a, b, c, 1992, 1994). An “in situ” synthesis was used to get Cd- or Pb-doped xerogel, and metal sulfide nanocrystals were obtained by reaction with H_2S at room temperature. The sulfide nucleation and growth were possible because of the high porosity of the gel, which allowed the reacting gas to react with metal ions dispersed in the silica network. A different approach was based on the addition of the anion precursors in the starting sols, and by precipitating the dispersed phase upon thermal treatment in a reducing atmosphere, to avoid oxidation of the chalcogenides (Tohge et al. 1992). A disadvantage of both these methods is that the porous xerogel exposes the non-oxide NPs to oxygen and, therefore, to oxidation. On the other hand, the densification achievable at temperatures higher than 1,000 °C leads to transformation of the nanoparticles, both in size and composition.

A solution to this problem is the use of matrices able to sinter at lower temperatures, as demonstrated by Takada et al. (1992) who used a borosilicate composition able to fully densify below 600 °C. Also hybrid organic–inorganic sol-gel matrices with lower porosity may have a similar effect (Guglielmi et al. 1994). An interesting nanocomposite material based on a hybrid organic–inorganic ureasilicate matrix and CdS nanoparticles was prepared by Boev et al. (2004) by the formation of amorphous clusters of CdS, through reaction of cadmium nitrate with thioacetamide, $\text{C}_2\text{H}_5\text{NS}$, in a ureasilicate sol. The hybrid matrix was obtained using an organically modified silicon alkoxide and a diamine functionalized oligopolyoxyethylene, which formed a rubberlike material composed of a siliceous network grafted through urethane groups to both ends of poly(oxyethylene) glycol segments (Goncalves et al. 2002). The final material, which didn’t require any heat treatment, was transparent, homogeneous and flexible, and dense enough to prevent further aggregation and sedimentation of the CdS colloidal phase.

A different strategy to protect the non-oxide nanocrystals from oxidation is to fill the pores by further impregnation of the porous xerogel with the sol (Piñero et al. 1994; Litrán et al. 1997), but it was found that the impregnation process influences the xerogel evolution, becoming an important step for the control of the final microstructure (Hummel et al. 1997).

The examples given above show that the “in situ” approach is useful and relatively simple, but the interference of various chemical processes occurring at the same time in the same batch is difficult to control, especially with respect to the size and size distribution of nanoparticles.

An “ex situ” approach, based on the addition of already-synthesized NPs to the sol, was proposed to avoid these problems (Spanhel et al. 1992). An example is given by the synthesis of CdS or PbS quantum dots by reaction of Cd or Pb acetates with thioacetamide in presence of a mercaptosilane and the subsequent addition of the colloidal sol to the matrix precursor sol (Guglielmi et al. 1997; Martucci et al. 1999a, b). A homogeneous distribution in the matrix, with controllable particle diameter between 2 and 5 nm, and narrow size distribution were easily obtained (Fig. 7).

This approach is very flexible and allows the synthesis of complex multifunction systems. An example has been experienced by the authors with the preparation of a material which was required to have high transparency in the visible range, tunable refractive index, luminescent properties, and being suitable for imprinting lithography and aerosol printing technologies (Antonello et al. 2011). The problem was afforded by designing a hybrid organic–inorganic matrix containing titanate nanosheets to increase the refractive index and CdSe@ZnS core-shell quantum dots to tune the photoluminescence properties. The two types of nanoparticles

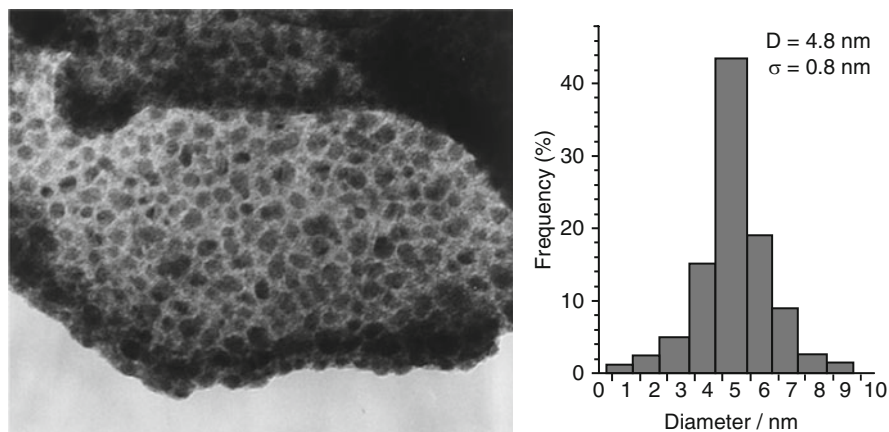


Fig. 7 HRTEM micrograph of a zirconia ormosil film doped with 10 mol% PbS and histogram of PbS particle size distribution (Reprinted from *J Non-Cryst Solids*, 244, Martucci A, Innocenzi P, Fick J, Mackenzie JD, Zirconia-ormosil films doped with PbS quantum dots, 1999b, with permission from Elsevier)

were synthesized separately following specific protocols, but in both cases 6-amino-1-hexanol was used to functionalize the surface of the nanoparticles and to allow them to link to the matrix network.

Nanocomposites with Polymer Matrix

Nanocomposites with a polymer matrix, where sol-gel has been used to obtain oxide nanoparticles dispersed in the macromolecular organic network, are of great interest because their mechanical properties may be significantly improved. It is well known that in traditional composites, the mechanical properties (i.e., the elastic modulus) are modified by the filler. With nanofiller it should be possible, in principle, to get much higher effects with smaller fraction due to the exceptionally high surface to volume ratio of nanoparticles and/or, in some cases, the extremely high aspect ratio. This would be true, however, only in the case of a homogeneous dispersion of the dispersed phase in the polymer and a good interaction between the two phases. Therefore, the molecular control of the metal oxide/polymer interface is the key for success.

A possible “in situ” strategy is based on the contemporary occurrence of hydrolysis and condensation reactions of the inorganic precursors and the organic polymerization. The possible interactions between the two processes have been described by Kickelbick (2008). They may be summarized as follows:

- (a) The alcohol molecules present in the system or produced in the hydrolysis of alkoxides may behave as chain terminators in anionic polymerizations.
- (b) Initiators and chain ends may act as nucleophile species and lead to substitution reactions at the metal alkoxide, resulting in chain termination.
- (c) Some groups present in polymers (i.e., ethylene oxide in PEO) interacts with the water molecules necessary for the hydrolysis in the sol-gel process, thus affecting the kinetics of gelation.

The compatibility between the inorganic phase and the polymeric one may be controlled in different ways, for example, using “compatibilizing” solvents. An example is given by *N,N*-dimethylformamide or *N,N*-dimethylacetamide that forms hydrogen bonds with silanol groups of the silica network and is highly compatible to organic polymers.

Polymers can also be modified by functionalizing their ends or the backbone with groups that increase the interaction between the organic and the inorganic components. Depending on the effectiveness of the interaction, it is possible to drive the process to give a homogeneous hybrid system or a nanocomposite.

Due to the interactions among the different chemical species in the system, the process must be optimized, also from the point of view of the sequence of addition of the reactants.

Hirano and co-workers demonstrated that if the organic polymerization precedes the hydrolysis and condensation reactions, the composite will be made of small

particles, but if the hydrolysis is run before the polymerization, larger particles are obtained (Yogo et al. 1994; Hirano et al. 2001, 2003).

Many papers have been published on the synthesis of polyimide (PI)/SiO₂ nanocomposites. This is a special case, indeed, as different aspects make the synthesis relatively simple. Polyamic acid (PAA), which is the precursor used for the polymer matrix, can tolerate the water necessary for the sol-gel reactions, and the imidization reaction, which converts PAA to a polymer, is not affected by the inorganic phase generated by the hydrolysis of the alkoxide. Furthermore, the excellent thermal stability of polyimides makes possible the heat treatment of the composite up to 350 °C, allowing the inorganic network to increase its connectivity. Also in this case, however, the obtainment of nanometer and well-dispersed particles is not trivial. The interaction between the inorganic and the organic phases must be pursued through specific strategies: using polyamic acid containing pendent hydroxyl groups (Huang and Gu 2003) or siloxane functionalities (Park et al. 2002), which partially crosslink with the inorganic network, or using γ -glycidoxypropyltrimethoxysilane (GLYMO) as a compatibilizer to enhance the interchain interaction (Musto et al. 2004; Kizilkaya et al. 2010). Figure 8 shows the difference in the microstructure of the nanocomposite adopting or not a compatibilizer.

Li et al. (2007) demonstrated that also in the case of PI/silica nanocomposites the order by which the chemicals are introduced in the batch may have a large effect on the size of the particles in the matrix.

The better compatibility and interfacial strength between silica nanoparticles and the polyimide matrix bring to better mechanical properties, as demonstrated by Chen et al. (2004). The best performances were obtained with 10–15 wt% silica and the use of GLYMO, which allowed the formation of chemical bonds between the hydroxyl groups of the polymer and the epoxy groups of GLYMO. The maximum tensile strength increased from 65 to 90 MPa, and the maximum elongation at break increased from 7% to 10%. For a review on this subject, see Ragosta and Musto (2009).

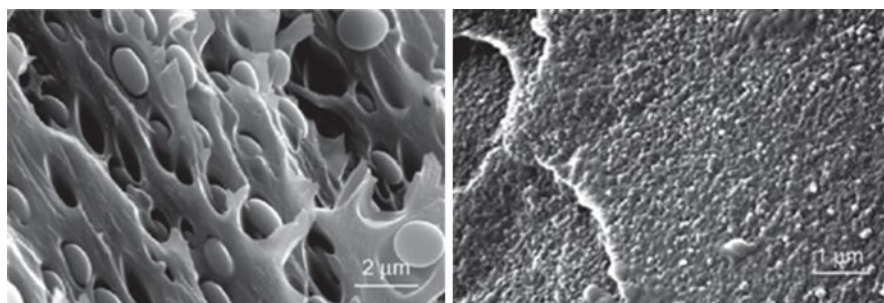


Fig. 8 Different microstructures obtained in polyimide/SiO₂ nanocomposites by using (*right*) or not (*left*) GPTMS as a compatibilizer (Polymer, 45, Musto P, Ragosta G, Scarinzi G, Mascia L, Polyimide-silica nanocomposites: spectroscopic, morphological and mechanical investigations, 1697–1706, 2004, with permission from Elsevier)

An interesting example of interaction between the reactions leading to the organic and the inorganic polymerization, and the possible strategy to avoid it, is offered by nanocomposites based on polyurethane hybrid matrices and was described by Becker-Willinger (2014). Isocyanate polymerization may be affected by side reactions with small nucleophilic molecules such as water and amines, resulting in less cross-linking and affecting the mechanical properties in the final material. This effect may be reduced by blocking the electrophilic reactive functionalities of isocyanate molecules with molecules having a moderate nucleophilic character, thus protecting them from undesired side reactions. The bond between the isocyanate and the blocking molecule has to be strong enough to stabilize the sol before its application, but it must be cleavable during the final curing of the material.

Further examples are rubbers reinforced with silica nanoparticles (Ykeda et al. 1997, Ykeda and Kameda 2004; Kohjiya and Ykeda 2003). Raw rubber or rubber vulcanizate may be swelled in tetraethoxysilane (TEOS), which is then transformed into silica by sol-gel reactions. In this case, the dispersed phase is synthesized within the matrix. A homogeneous distribution of nanoparticles is obtained, and mechanical performances are better with respect to the same nanocomposite obtained by mechanical mixing.

Applications of Sol-Gel Nanocomposites

The development of sol-gel nanocomposite materials has been mainly driven by their potential use in many applications, and commercial sol-gel nanocomposites are already part of manufacturing technology. It is possible to define a commercial product as the one that is both offered for sale and used in the regular production of a device or item in general commerce, as already pointed out by B. Arkles (Arkles 2001). In this chapter, we present examples of sol-gel nanocomposites that potentially can have commercial application, based on the literature of the last 10 years.

Biomaterials

Sol-gel nanocomposites are widely used as biomaterial (e.g., for drug delivery systems, cell encapsulating matrices, and artificial bone substitutes) because of their controllable physicochemical properties including size, morphology, composition, and microstructure and also for their controllable biocompatibility and biodegradability. A biomaterial can be defined as any matter, surface, or construct that interacts with living systems.

Bioactive glasses were first developed by Hench and co-workers in 1969 (Hench et al. 1971) and represent a group of surface reactive materials which are able to bond to bone in physiological environment (Boccaccini et al. 2010). Bioactive glasses most widely used in biomedical applications consist of a silicate network incorporating sodium, calcium, and phosphorus in different relative proportions. For

example, 45S5 bioactive glass universally known as Bioglass[®] has a composition of 45% SiO₂, 24.5% Na₂O, 24.5% CaO, and 6% P₂O₅ in wt.%.

To provide additional functionality, glass and glass-ceramic matrices are combined with synthetic and natural polymers such as poly(L-lactic acid) (PLA), poly(lactic-co-glycolic acid) (PLGA), and polycaprolactone (PCL). Peter et al. (2010a) fabricated bioactive glass-ceramic nanoparticles via the sol-gel process, which were blended with chitosan and gelatin to obtain composite scaffolds having macropores of 150–300 μm in diameter. The obtained scaffolds showed better degradation and swelling properties, increased protein adsorption, and very good cell attachment and spreading, with increasing the bioactive nanoparticles content. The scaffolds were proposed as potential candidates for alveolar bone regeneration applications. Xu et al. (2011) synthesized porous glass-collagen-phosphatidylserine (BG-COL-PS) nanocomposite scaffolds via the freeze-drying technique. The scaffolds had interconnected porous structures with pore diameter up to about 300 μm and with 75% in porosity. According to the culturing rat mesenchymal stem cells, the presence of PS stimulated osteogenic differentiation. Boccaccini et al. (2005) fabricated the tubular foam scaffolds of PLGA/ Bioglass[®] composite for tissue engineering scaffolds for the regeneration of tissues requiring a tubular shape scaffold, such as intestine, trachea, and blood vessels. Maquet et al. (2004) fabricated highly porous scaffolds based on PLGA obtaining polymer foams containing 45S5 Bioglass[®] by freeze-drying procedure. The presence of the filler retarded the degradation of the scaffolds while it stimulated apatite deposition.

Hong et al. (2009) have investigated a new family of composites combining PLA and sol-gel-derived bioactive glass-ceramic (BGC) nanoparticles. 3D porous scaffolds were prepared by thermally induced phase-separation combining PLA and different concentrations of BGC nanoparticles. The *in vitro* studies showed that composites containing BGC nanoparticles with lower phosphorous and higher silicon content have better bioactivity than those with lower silicon and higher phosphorous content. More recently, El-Kady et al. (2010) have developed sol-gel-derived bioactive glass nanoparticles/PLA composites by using solid-liquid phase-separation method combined with solvent extraction. They used a modified alkali-mediated sol-gel route to obtain bioactive glass nanoparticles. The modified sol-gel method resulted in reduction of the gelation time to about a minute rather than days as in the traditional sol-gel process.

Furthermore, fast gelation prevented the aggregation and growth of colloidal particles to sizes larger than 100 nm. The proposed method is thus capable of delivering nanoparticles of sizes less than 100 nm with minimum agglomeration. It was reported that the scaffold's pore size decreased with the increase in the glass nanoparticles content. The *in vitro* studies revealed that the addition of bioactive glass nanoparticles improved the bioactivity of the scaffolds.

Natural-based materials such as polysaccharides (starch, chitin, chitosan) or proteins (silk, collagen) can be used as polymer matrices to prepare sol-gel nanocomposites. Peter et al. (2010b) have synthesized scaffolds made of SiO₂-CaO-P₂O₅ bioactive glass-ceramic nanoparticle and chitosan by using lyophilization technique. The developed composite scaffolds demonstrated adequate swelling and

degradation with the addition of the nanoparticles. *In vitro* studies showed the deposition of apatite on the surface of the composite scaffolds, indicating the bioactive nature of the composite scaffolds. The investigation of the *in vitro* behavior considering osteoblast-like cells (MG-63) indicated that cells attached on the pore walls of the scaffolds and showed initial signs of spreading.

A series of composites of various morphologies, such as fibrous membranes and 3D porous scaffolds, were developed by compounding polymers and bioactive glass nanofiber. Kim et al. (2006a) were the first to develop a composite of PLA filled with sol-gel-derived bioactive glass as a nanoscale composite fiber by means of electrospinning. Nanocomposites with a dense nanofibrous network were achieved. It was observed that glass nanofibers were uniformly dispersed in the PLA matrix. The excellent bioactivity of the nanocomposite was confirmed *in vitro* within a simulated body fluid by the rapid induction of bonelike minerals onto the nanofiber surface. Kim et al. (2006b) also developed bioactive glass nanofiber collagen nanocomposite both in the form of a thin membrane and as macroporous scaffold.

Chemical Sensors

Sol-gel nanocomposites are widely used as sensitive material in chemical sensors.

Sol-gel is relatively simple to transfer to an industrial scale and is particularly suitable for the deposition of thin films, as it is based on the deposition of a thin layer of the liquid precursor solution over a substrate at room temperature (by dip-coating, spin-coating, spraying techniques), followed by a thermal treatment. In the case of thin films, where the cost of precursors is minimized, the method is also not expensive. For these reasons, sol-gel may offer interesting challenges in the field of chemical sensors, and indeed it is actually largely investigated.

An example of the potentiality of the sol-gel method is offered by the synthesis of nanocomposite thin films constituted of a nanoporous amorphous silica matrix and homogeneously distributed semiconducting metal oxide and/or metal nanoparticles. The nanoporosity provides the path for gas molecules to reach all the volume of the sensing material and the possibility for the nanoparticles to be efficiently exposed to the analyte. Based on this strategy, Guo and Tao (2007) developed ammonia optical sensors by coating an optical fiber with porous silica film containing Ag nanoparticles. In this case, the interaction of the NH_3 gas induces a variation of the surface plasmon resonance peak of the Ag nanoparticles.

Hasani et al. (2010) dispersed highly luminescent CdSe@ZnS core-shell quantum dots in hybrid organic–inorganic sol-gel matrix obtained from tetramethoxysilane and 3-aminopropyltriethoxysilane. The quenching of the luminescence of fragment of the nanocomposite xerogel has been monitored in the presence of different volatile organic compounds. Martucci et al. were the first to develop optical gas sensors based on metal oxide nanoparticles (NiO or Co_3O_4) dispersed in a porous SiO_2 sol-gel film (Martucci et al. 2004a, b). The optical transmittance of the nanocomposite films increases upon exposure to CO or H_2 gas due to the interaction of the gas

molecules with the adsorbed oxygen on the metal oxide nanoparticles surfaces. The sensor sensitivity and selectivity have been improved by the addition of Au nanoparticles, which catalyze the reaction with the target gases and modified the absorbance spectrum. In fact the presence of the Au surface plasmon resonance peak permits to selectively recognize H₂ and CO due to the wavelength dependence of the gas-induced optical transmittance variation (Buso et al. 2007b). Moreover by tailoring the thermal annealing conditions, it was possible to synthesize cookie-like Au/NiO nanoparticles showing unique structural and optical properties (Mattei et al. 2007).

The high loading of metal oxide nanoparticles in the SiO₂ matrix (up to 40 mol%) obtained by Martucci et al. (Cantalini et al. 2005; Della Gaspera et al. 2010b) allowed the realization also of conductometric gas sensors. They synthesized NiO, Co₃O₄, and SnO₂ nanocomposite films which have shown a p-type (NiO and Co₃O₄) and an n-type response (SnO₂) with greater sensitivity to H₂ gas than CO and a detection limit of 10 ppm.

Buso et al. (2007b) developed TiO₂ sol-gel films containing Au nanoparticles for CO and H₂ optical and electrical gas sensors. The authors present outstanding dynamics for hydrogen detection and a CO response dependent on the amorphous or crystalline (anatase) phase of the TiO₂ film.

Recently Lu et al. (2011) synthesized SiO₂-graphene oxide nanocomposite decorated with Ag nanoparticles that can be used as biosensor for the glucose detection in human blood serum.

Catalysis

Catalysis is the increase in the rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents in the chemical reaction, a catalyst is not consumed. With a catalyst, less free energy is required to reach the transition state, but the total free energy from reactants to products does not change. The production of most industrially important chemicals involves catalysis. Similarly, most biochemically significant processes are catalyzed.

For example, Pagliaro et al. (2011) synthesized sol-gel catalyst made of nanostructured Pd organosilica xerogels suitable for the catalysis of carbon-carbon bond formation in relevant organic reactions. Such nanocomposite has been commercialized with the trademarked *SiliaCat Pd⁰ Hydrogel*. Recently Sabada et al. (2014) developed a nanocomposite catalyst for the conversion of xylose to furfural based on aminopropyl-functionalized SiO₂ sol-gel nanoparticles embedded in poly(styrenesulfonic acid).

Photocatalyst is a catalyst that participates and modifies the reaction rate of chemical reactions under light irradiation. Since the discovery that TiO₂ particles were capable of trapping and oxidizing organic compounds to minerals and small molecules such as CO₂, extensive studies have been conducted to explore the potential of TiO₂ as photocatalyst for environmental decontamination such as water purification and air cleaning. Nanocomposite based on TiO₂ has been studied extensively because they can have better performances than pure TiO₂.

Li et al. (2010) synthesized mesoporous silica-supported Cu/TiO₂ nanocomposites through a one-pot sol-gel method for the photoreduction of CO₂ to hydrocarbons. The high surface area mesoporous silica substrate (>300 m²/g) greatly enhanced CO₂ photoreduction, possibly due to improved TiO₂ dispersion and increased adsorption of CO₂ and H₂O on the catalyst.

Carbon nanotube/TiO₂ nanocomposites were fabricated by Gao et al. (2008) by a surfactant wrapping sol-gel method that led to a uniform and well-defined nanometer-scale titania layer on individual carbon nanotube. The nanocomposites were found to enhance the initial oxidation rate of methylene blue by onefold compared to the pure TiO₂ sample. This larger degree of rate enhancement is attributed to the supporting role of the carbon nanotubes and surface properties.

Ag-TiO₂ nanocomposites have been used as bactericide material, and recently it was demonstrated a long-lasting antibacterial activities of Ag-TiO₂ nanocomposite sol-gel thin films under solar light irradiation (Akhavan 2009).

Wettability

The wetting properties of a surface can be modified with appropriate surface coating which can impair desired wettability by tailoring the surface energy: lowering the surface energy, it will lower the wetting of the surface. Hydrophobic surfaces are those for which water is not wetting (spreading) the surface. Materials with very low surface energy are, for example, polydimethylsiloxanes (silicone) and polytetrafluoroethylene (PTFE, Teflon[®]) with surface energies below 18 mN/m.

Xu et al. (2010) developed a superhydrophobic (water contact angle larger than 150°) highly transparent and stable organic–inorganic nanocomposite coating by a simple sol-gel dip-coating method. This method involves control of the aggregation of sol-gel SiO₂ particles by polymerization and ultrasonic vibration to create a nanocomposite coating made of silica nanoparticles functionalized with aminopropyltriethoxysilane. Superhydrophobicity and transparency of the coating can be controlled by adjusting the initial concentration of monomer and the size of aggregates in the sol-gel. Thus, superhydrophobicity and high transparency can be concurrently achieved in a single coating.

Lakshmi et al. (2012) studied the effect of the size of silica nanoparticles on the wetting properties of sol-gel nanocomposites obtained from methyltriethoxysilane. The coatings became superhydrophobic at an optimum silica concentration. The water repellence was further improved by the addition of fluoroalkylsilane (FAS). The optimum silica concentration was found to depend on the size of silica nanoparticles and FAS content. The superhydrophobic property of the coatings was due to the synergistic effect of surface chemistry and surface microstructure.

Hao et al. (2012) used sol-gel nanocomposites made of polyhydromethylsiloxane and silica nanoparticles for developing superhydrophobic cotton fabric with favorable washing durability, maintaining its air permeability, color, and softness.

Gao et al. (2014) developed a separation thin membrane made of single-walled carbon nanotube coated with sol-gel TiO_2 that has superhydrophilic and underwater superoleophobic properties after UV-light irradiation. The robust and flexible nanocomposite films with a thickness and pore size of tens of nanometers can separate both surfactant-free and surfactant-stabilized oil-in-water emulsions in an ultrafast manner.

Scratch-Resistant Coatings

Hard coating is one of the most studied applications for sol-gel nanocomposites coating, and it is one of the most promising for industrial application as pointed out by Sепeur and Frezer (2014). They reported that for a good abrasion resistance, the coating thickness of a cured sol-gel layer must be in the range between 3 and 20 μm . In fact, below 3 μm no significant increase in scratch resistance is observed, because the influence of the substrate. At a coating thickness of more than 20 μm , the inflexibility of the sol-gel coatings leads to cracks and poor adhesion on the substrate. In general, hard coating is based on SiO_2 , Al_2O_3 , ZrO_2 , or TiO_2 as network formers or fillers in the form of nanoparticles and organic-modified silanes such as epoxysilanes, methylsilanes, methacrylsilanes, and vinylsilanes.

For example, Yuan et al. (2005) studied the influence of the size of SiO_2 nanoparticles functionalized with 3-glycidoxypropyltrimethoxysilane on the hardness of the nanocomposite coating deposited on aluminum substrate. More recently, Sowntharya et al. (2012) developed hybrid nanocomposite coatings from titanium tetraisopropoxide and epoxy- or acrylic-modified silanes for improving the resistance to scratch of polycarbonate substrate. The scratch as well as abrasion resistance increases as a function of coating thickness. The pencil scratch hardness improves from 2B for the bare PC to a maximum of 3H for the coating obtained from an aged sol derived from epoxy modified silane.

Conclusion

Nanocomposites can be prepared by the sol-gel method in different ways and with different strategies. The general principles for their synthesis have been shortly discussed considering “in situ” and “ex situ” methods and different types of nanocomposites, with the matrix, the dispersed phase(s), or both obtained from sol-gel. The synthesis methods are discussed for nanocomposites with an oxide, with a hybrid organic–inorganic or a polymeric matrix, and with oxide, metal, or non-oxide nanoparticles. Representative examples of nanocomposites that potentially can have commercial application are described in the second part of the chapter, based on the literature of the last 10 years.

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