Chemical Routes in the Synthesis of Nanomaterials Using the Sol–Gel Process

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ABSTRACT
In this Account, we discuss the usefulness of the sol–gel process in the synthesis of materials comprising nanoscale architectures. We describe the processing of semiconducting, metallic, ferroelectric, or scintillating nanoparticles in various oxide matrices. We also discuss the synthesis of some nanoporous oxides and organic–inorganic nanohybrids, including core–shell nanostructures.

Introduction

The growing interest in nanostructured materials calls for the development of processing techniques that allow for the tailoring of specific features of the nanometer size. One method for engineering such structures involves the chemical manipulation of nano-building blocks. Obviously, because traditional processing of ceramics involves grinding, pressing, and heating powders in the micrometer range, engineering such nanostructures through traditional approaches is a very challenging materials science problem. The growth of nanocrystallites from glass melts may be one of the few demonstrated successes of traditional ceramics processing in this context. The synthesis of nanocrystalites of metals or semiconductors through a method known as "striking a glass" comes to mind, as well as the synthesis of partially stabilized zirconia, in which metastable nanoparticles, tetragonal ZrO_2, are grown in a cubic matrix. Recently, with the advent of the sol–gel as a low-temperature alternative processing method using chemical processes in the liquid state, novel processing strategies and therefore materials have emerged. When such reactions are properly controlled, they lend themselves extremely well to the synthesis of nanomaterials, for the obvious reason that they involve molecules of the appropriate size and mobility in the liquid state. Therefore, the process offers the chemist a unique opportunity to design and engineer original and novel nanomaterials. In this Account, we summarize several sol–gel strategies that have been successfully used to engineer nanostructure glasses or ceramics. Some of them take advantage of the

versatility and complexity of the hydrolysis and condensation reactions of metal alkoxides, others exploit the nanoporosity of gels as a host for various molecules or inorganic clusters. In all cases, the chemistry of the systems is the main controlling factor for the resulting nanostructure. Examples discussed are nanoporous silica, semiconductor, ferroelectric, metallic, and oxide nanocrystallites in glass, as well as organic–inorganic nanohybrids.

1. Nanoporous Oxide Gels

The sol–gel process is generally described as a chemical route for the synthesis of ceramics.[1] It has been widely used in the processing of oxides as bulk, fibers, or coatings. The synthesis of SiO_2 from liquid silicon metal–organic precursors is probably the oldest and most investigated sol–gel process. Typically, it involves hydrolysis and condensation of a metal–organic precursor, such as tetraethoxysilane, in an appropriate solvent, such as ethanol, with or without the use of a catalyst. As these reactions proceed and the viscosity of the solution increases, a gel is formed. It is typically made of Si–O–Si bonds, forming a network within which reaction products are trapped. When such products are removed via evaporation, a nanoporous structure results. Pore size, distribution, and interconnectivity are affected by processing parameters, such as the type and amount of solvent and/or catalyst, temperature, and in some cases, the presence and arrangement of templating molecules. By themselves, these porous gels constitute a very interesting class of nanomaterials. The nanoporous architecture may be tailored for connectivity, orientation, arrangement, or size and exploited for various applications, such a chromatography columns, sensors, catalyst support, low dielectric constant materials, or controlled release of reactants. A very good review by Klein and Woodman lists the many different methods that can be used in SiO_2 synthesis and the effects of processing parameters on porosity.[2] The pores can later be impregnated and functionalized with a dye or organic molecule if they are interconnected. This material is really the "backbone" of the chromatography industry. The nanoporosity of these gels can also be exploited for many other purposes. For example, low dielectric constant materials can be made using tetramethyl ammonium silicate (TMAS), a structuring agent used in zeolite synthesis. Porosity at 50% and uniform pore-size distribution (average pore size of 40 Å) silica films have been obtained, yielding a material with a dielectric constant of 2.5.[3] A more recent development in the engineering of nanoporous materials is the use of templating molecules.[4] Using surfactant micelles as pore-forming agents, 65 vol % nanoporous dielectric films with a uniform pore size smaller than 5 nm were obtained. Tetraethoxysilane (TEOS) and surfactants were mixed in an acidic aqueous environment. During spin coating, the solvent was rapidly removed and the surfactant molecules formed micellar

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aggregates. After the surfactant was removed, a highly porous silica film resulted with controlled porosity and pore sizes. When proper dehydroxylation treatments were applied, stable, low dielectric constants of 1.8–2.2 were obtained.[5]

This approach, to some extent, derives from the very successful use of self-assembling molecules in the synthesis of mesoporous materials This field is now is a well-established and active area of research. It is possible to restrict one or more dimensions of mesoporous silica to facilitate mass transfer in adsorption or catalysis, thereby creating an ordered nanoporous structure. Nanoporous "lotus-like" silica flakes were obtained using a TEOS-based solution containing pores of 24 nm. The flakes exhibited superior performance in adsorbing biomolecules.[6] Other nanoporous oxide gels have been made using self-assembly. Mesoporous silicas with variable pore size and architecture have been made using block copolymers with one polyelectrolyte block as templates. Pore size and connectivity follow the structure of the block copolymer micelles or mesophases; i.e., the resulting silica gel network is a precise copy of the original self-assembly structure. Dependent upon the relative block lengths and the salt content in the reaction mixture, different aggregation structures are obtained, leading to well-defined spherical pores in the size range between 10 and 50 nm or more complex architectures, such as "rattles", the casts of multilamellar vesicles.[7] More complex and original structures may be obtained. Schlottig et al., for example, used tetraethoxysilane, ethanol, water, and HCl mixed in three different molar ratios and stirred for 3 h at room temperature to obtain an array of closed SiO_2 nanotubes. Pores of alumina membranes were filled using both spin- and dip-coating procedures. After a partial removal of the alumina (5 min in NaOH) from the coated membrane, nanotubes were observed.[8]

2. Nano Organic–Inorganic Hybrids (Dyes, Proteins, and Polymers) in Gels

As discussed above, a gel derived from a sol–gel process is nanostructured in the sense that it exhibits porosity in the nanometer range. In some cases, the porosity of the gel developed around a templating organic molecule, such as a surfactant; in others, the porosity was the result of evaporation of reaction byproducts. In any case, one of the advantages of the sol–gel route is that the low processing temperatures allow for the coexistence of organic and inorganic constituents within the same matrix. In traditional ceramic processing, this is prevented by the high temperatures required by processing the oxide matrix. In this section, we focus on the role of organic entities that reside within the oxide gel, either chemically bonded or adsorbed, but in any event adding functionality to it at the nanoscale. As such, these organic–inorganic hybrids represent a type of nanocomposite heretofore impossible to engineer. The organic entity may be placed within the inorganic matrix using one of two routes: either it is mixed into the sol–gel solution or it is impregnated

into the dry, porous gels. In the first approach, the organic entity may be chemically grafted onto the backbone or merely adsorbed onto the pore surface. In the second approach, the organic entity is assumed to adsorb on the surface of the pore.[9]

An organic dye molecule can be easily added to a sol–gel liquid solution. This was first reported by Avnir and co-workers for the dye Rhodamine 6G added to a TEOS alcoholic solution.[10] The dye molecules are uniformly dispersed in the TEOS solution. When gelation occurs, the dye molecules are trapped in the porous oxide gel matrix, forming an organic–inorganic nanomaterial. The original intent was to make organic dye lasers. The dyes were found to be generally stable within the oxide matrix. However, it was also found that the stability of many laser dyes was affected by ambient atmosphere, which highlights the role of porosity in these materials.[11] Many organic dyes have since been mixed with sol–gel solutions to create a variety of colored glasses tailored for various applications.[12] Other organic molecules have also been used for their sensing characteristics.[13]

Schmidt suggested that the structure of an oxide could be modified by polymeric chains.[14] He named the materials "Ormocers", for organically modified ceramics. Another term frequently used for these materials is "Ormosils", for organically modified silicates. Both terms will be used interchangeably here. Since this pioneering work, many kinds of organic–inorganic hybrids have been made. Covalent bonding between organic and inorganic entities may or may not exist. Figure 1 gives an example of the types of nanoarchitectural hybrids that can be made. A drying control chemical additive (DCCA), such as formamide or oxalic acid, may be added to the sol–gel solution to prevent shrinkage and cracking.[15,16] Hench[17] also found that, if large amounts of such organics were dissolved in a typical sol–gel solution of TEOS or tetramethoxysilane (TMOS) in alcohols, the average pore size as well as the pore diameters could be significantly reduced.

One interesting family of organic–inorganic nanocomposites is that based on the cubic silsesquioxanes.[18] The smallest conceivable nanopore in silica is probably the empty space at the center of a cube made of eight silica atoms, also called the H8T8 unit. Although this structure is rare in glass or traditionally processed silica, its derivative silsesquioxanes have attracted interest lately. These systems offer the advantage of a very clear definition of the inorganic nanophase. The inorganic phase is a well-defined silica core, rigid and completely defined. Eight organic groups can be appended to the vertexes of the cages, linking the cores to one another. The organic groups may have varying length and chemical composition. Nanohybrid networks in which oxide and organic networks interpenetrate one another can also be made.[19,20] In such materials, the organic and inorganic networks develop independently from each other and no covalent bond exists between them.

In some cases, it may be desirable to design a material in which a strong bond exists between the organic and inorganic phases. A typical example is the SiO_2–poly-
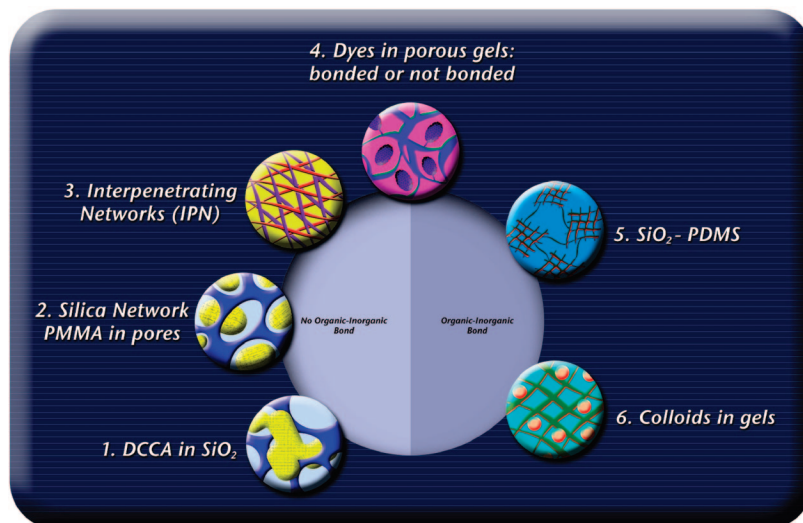
FIGURE 1. Various sol–gel-derived nanoarchitectures for sol–gel organic–inorganic hybrids. (Illustration: Luis Tinoco).
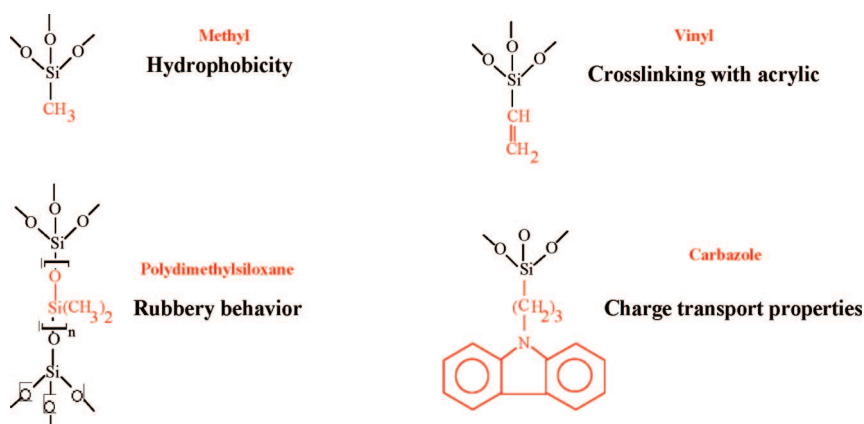

FIGURE 2. Various types of organic entities that may be grafted onto oxide backbones in type-II hybrids.

dimethylsiloxane (PDMS) system[21] that has been studied extensively in our group. The fundamental feature of this material is that both inorganic and inorganic phases consist of Si–O–Si chains that can be chemically linked during the sol–gel process. The compatibility between the silanol-terminated PDMS and TEOS has made the materials very attractive to many researchers.[22,23] This compatibility, as shown in the reaction below between a silanol-terminated PDMS chain and a molecule of silicic acid, is typical of the kind of reaction found in so-called "type-II" hybrids, where cross-linking between organic and inorganic components can take place:
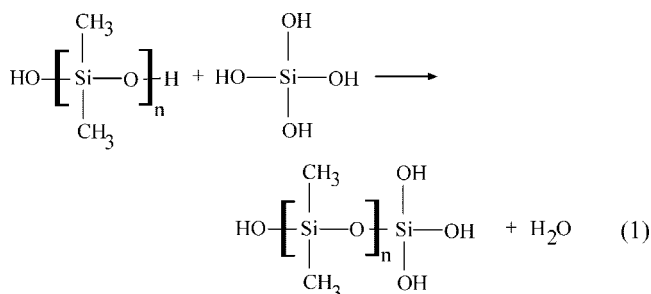
The advantages of this system include the similarity between the silica network and the siloxane structure and the high temperature stability of PDMS compared to other elastomers. Dependent upon solution conditions, such as acid or basic catalysis, pore structures and properties can be very different. The material can be either glassy or rubbery depending upon the weight fraction of the organic constituent. The structure, properties, and potential applications of these organic–inorganic materials have been reviewed.[24]

Various biological moeities, such as proteins or enzymes, have been incorporated into oxide matrices, particularly silica-based matrices. The oxide "nanocages" do not just accommodate the size of the protein, they also protect it from external attack while allowing the passage of reactants.[25] Various biological sensors have been fabricated using this approach. Examples of molecules that may be used in the synthesis of such hybrids are shown in Figure 2.

A schematic summary of these various organic–inorganic hybrid nanocomposites is shown in Figure 2. They can be divided into two broad categories, as described by Sanchez and Ribot: either the organic and inorganic constituents are covalently bonded or they are not. Structure 1 represents the case of the DCCA–SiO_2 nanohybrid, in which the DCCA has been trapped in the pores.
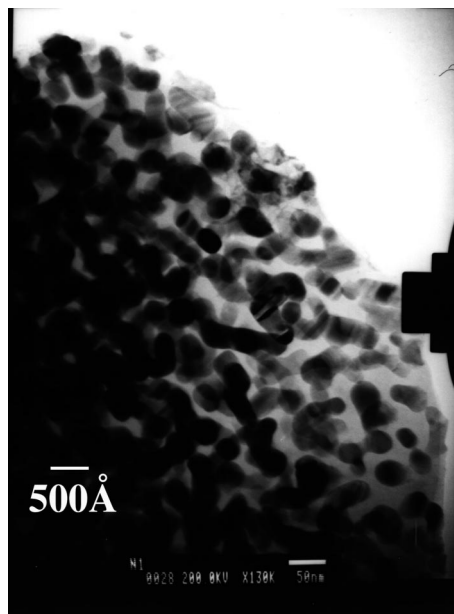
FIGURE 3. Lu_2SiO_5 nanoparticles in an optically transparent SiO_2 matrix.

FIGURE 4. (Top) Optically transparent, sol–gel-derived Lu_2SiO_5–SiO_2 scintillators. (Bottom) Wavelength distribution of scintillation light from LSO when excited with 356 nm of light at room temperature. The doublet structure corresponding to the Ce^{+3} ion transition from the 5d level to the two 4f ground states is mostly washed out at room temperature but can still be seen in these spectra.

Structure 2 represents the case of the poly(methyl methacrylate) (PMMA)–SiO_2, in which the PMMA has been polymerized *in situ* within the interconnected pores of the silica inorganic network.[26] Structure 3 shows the interpenetrating organic and inorganic (IPN) networks.[27] In structure 4, organic dyes or molecules are either covalently bonded (right) to the inorganic framework or not (left). In structure 5, PDMS and SiO_2 are covalently bonded. Dependent upon the weight fraction of PDMS, the material can be either rubbery or hard.[28] Structure 6 shows inorganic colloids, such as silica covalently bonded to a gel, as will be described later.

3. Nanocrystallites Obtained via Controlled Crystallization of Gels

Traditional glass ceramics have been known for decades. They are typically obtained by first forming a glass melt, quenching it, and heating it up to grow a crystalline phase within the glass matrix. If the particle size is kept below the wavelength of visible light, the glass ceramic is transparent. Many materials, such as optical filters, zero-thermal expansion coefficient materials for cooking ware, or telescopes, have been through this process. In many instances, the crystallite size must be kept in the nanometer range to achieve the desired properties. The sol–gel process offers an elegant alternative to this high-temperature approach because many amorphous oxide gels can now be made at or near room temperatures. This opens the possibility of growing a nanocrystallite within a matrix that contains organic entities. Several examples of the synthesis of nanomaterials from the controlled crystallization of gels are discussed below.

 a. Scintillating Nanoparticles. Scintillators are usually grown as large, transparent single crystals. Cerium-doped lutecium orthosilicate (LSO) is the most promising scintillato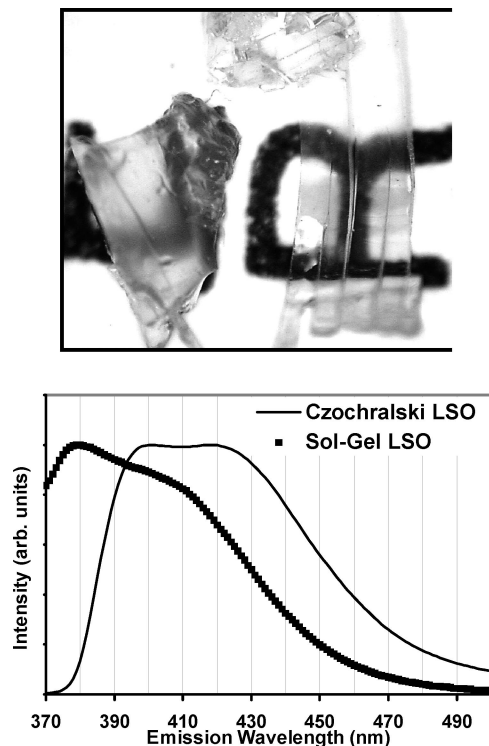r discovered in almost 5 decades. It exhibits a unique combination of important properties for X- and γ-ray spectroscopy: high density, fast decay, and large light yield. However, the practical use of LSO is hindered by difficulties related to its fabrication as a single crystal by the Czochralski method. We successfully used the sol–gel process to obtain lutecium silicate scintillators. The most challenging issue was to maintain transparency in the visible part of the electromagnetic spectrum in a polycrystalline material. As long as the size of the LSO crystals was kept below the wavelength of visible light, transparent scintillators were obtained. The nucleation and growth of the scintillating phase had to be controlled so that the particle size remains in the nanometer range. The process was based on the hydrolysis of lutecium alkoxides.[29,30] We found that there were two ways of limiting the size of Lu_2SiO_5 nanocrystallites: one was to maintain the Lu/Si ratio at low values, and the other was to limit the heat-treatment temperature. In summary, we found that, upon appropriate drying and firing, lutetium silicate crystals could be grown in a silica matrix and that, with careful control of the synthesis, the nanomaterial was transparent. The Lu_2SiO_5 particle size was approximately 200 Å (Figure 3). Light decay measurement and γ-ray spectral response were measured, and the polycrystalline sol–gel nanomaterials were found to be comparable to that of traditional LSO single crystals (Figure 4).

 b. Ferroelectric Nanoparticles In Inorganic Gels. Many ferroelectric oxide materials have been prepared by the sol–gel process.[31] In our group, we have studied the
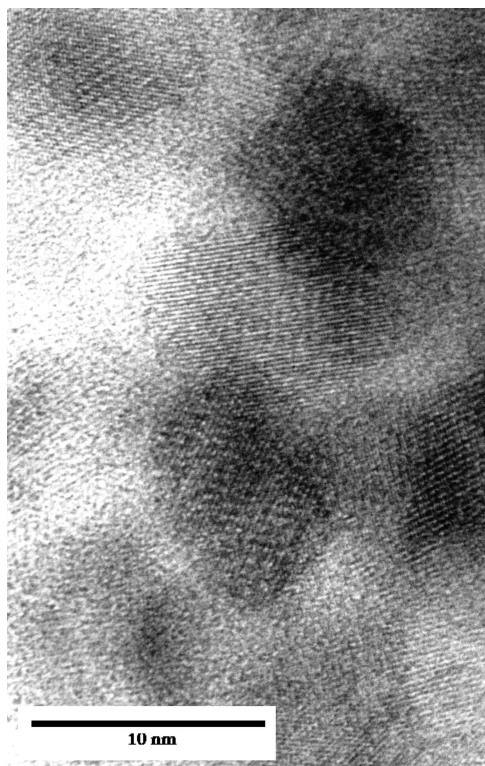
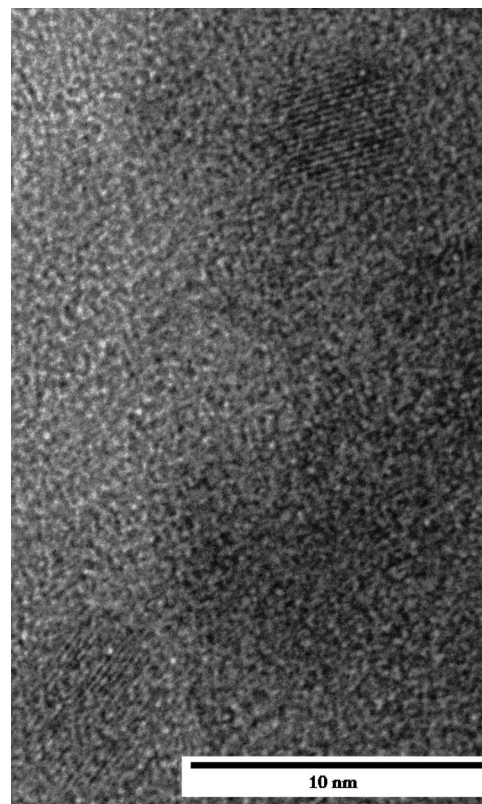**FIGURE 5.** BaTiO$_3$ nanoparticles in the SiO$_2$ matrix (heat treatment at 800 °C/2 h).

FIGURE 6. LiNbO$_3$ nanoparticles in the SiO$_2$ matrix (heat treatment at 200 °C/2 h).

FIGURE 7. LiNbO$_3$ nanoparticle in a TDP–SiO$_2$ Ormosil (heat treatment at 200 °C/2 h).

growth of nanocrystallites of ferroelectric phases from gels. With increasing temperature, local ordering of the ferro-electric oxides has been observed, starting with the formation on nanosize clusters at low temperatures. Such clusters have been called "ferrons" and have been shown to exhibit ferroelectric properties despite their small size. A theoretical model explaining the behavior of these "ordered clusters" was developed.[32] Similarly, ferroelectric crystals of LiNbO$_3$ and BaTiO$_3$ have been grown in an amorphous glass matrix of SiO$_2$ by the sol–gel technique. Such particles also grow in size and number with increasing temperature. Well-formed nanocrystallites of BaTiO$_3$ have been observed after heat treatment for 2 h at 800 °C (Figure 5). At temperatures as low as 200 °C in the case of LiNbO$_3$, some local ordering in the microstructure has been observed as well (Figure 6). The smallest observed size of these ordered entities is on the order of 3 nm. Despite the small size of the crystals, ferroelectric properties and P–E loops were observed.

In Ormosils. As noted above, the low processing temperatures of the sol–gel process open the possibility of growing an oxide phase within an organically modified matrix. We investigated the growth of LiNbO$_3$ in an Ormosil matrix containing a covalently attached organic molecule with high hyperpolarizability, such as triethoxy-silylpropyl dinitrophenylamine (TDP). At temperatures as low as 200 °C, below the decomposition temperature of the organic, LiNbO$_3$ ferrons have been observed (Figure 7). Interactions between organic and inorganic phases can take place. For example, we have observed that the strong bathochromic red shift observed when a TDP molecule
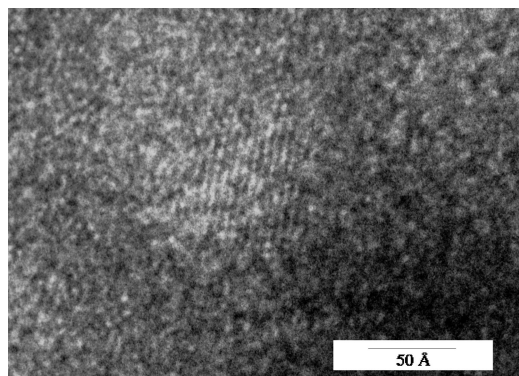
is exposed to a barium titanium alkoxide solution is still present after ferrons have formed. Other possible organic/inorganic interactions are possible and have yet to be investigated. At a minimum, ferroelectric properties have been observed in these organic–inorganic nanohybrids.[33,34] An idealized structure of such hybrids is shown in Figure 8.

4. Semiconducting Nanoparticles

For several nonlinear optical applications, it is often desirable to grow nanoparticles of semiconducting materials within optically transparent matrices. Table 1 lists the Bohr radii of several semiconductors. To observe
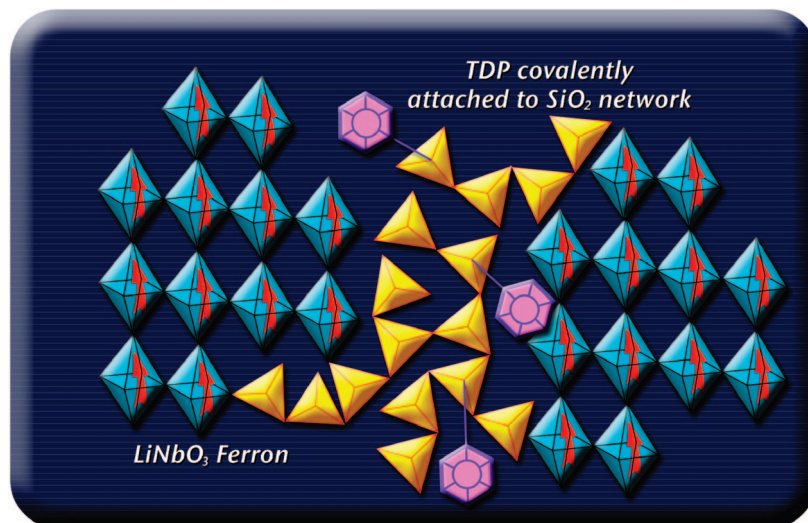
FIGURE 8. Schematic structure of a TDP–LiNbO$_3$ ferroelectric Ormosil nanocomposite. (Illustration: Luis Tinoco).

Table 1. Bohr Radii of Several Semiconductors

semiconductor	r_B (Å)	E_g (eV)
CdS	28	2.5
CdSe	53	1.7
CdTe	75	1.5
GaAs	124	1.4
PbS	180	0.41

quantum confinement, particles must be smaller than the Bohr radius of the electron-hole pair, typically less than 200 Å.

The sol–gel approach has been successfully used to synthesize such nanomaterials. Typically, a gel is obtained from the appropriate precursors, and the gel is subsequently heat-treated in a sulfidizing or reducing atmosphere to grow the semiconducting phase.

We have synthesized and compared the behavior of CdS-doped glasses, namely, a sodium borosilicate glass, obtained using TMOS, TEOS, boron ethoxide, and sodium acetate as precursors, and an ORMOSIL glass, obtained from a TEOS/PDMS system. A typical processing route is shown in Figure 9. Cadmium was introduced into the two solutions as cadmium acetate and cadmium nitrate, respectively. The film was exposed to H$_2$S gas after drying to form CdS crystals (up to 20 wt %). As a further refinement of the approach, 3-aminopropyltriethoxysilane (APTES) was also added to both solutions to provide enhanced control of the particle size and particle size distribution. Samples treated with APTES had smaller crystal particles with a narrower size distribution (2.8 nm average size, with a 0.9 nm standard deviation) (Figure 10). APTES helped anchor the dopant to the silica network of the glass, thereby avoiding precipitation of the salt during the sol–gel drying process. Of course, other more complex processing routes are possible. $\chi(3)$ values of about 10^{-6}–10^{-8} esu were observed in these materials. Channel waveguides were made by ion exchange in the sodium borosilicate glass, and propagation of 110 fs long pulses resulted in narrowing and spectral modulation of the input pulse.[35] Other semiconductor quantum dots,

such as CdTe (Figure 11),[36] SbSI,[37] or PbS,[38,39] have been successfully grown in oxide matrices using similar sol–gel processes.

5. Metallic Nanoparticles

As in the case of semiconducting nanoparticles, metallic nanoparticles in oxide matrices can exhibit interesting optical properties. While nanoparticles of metals in glass have been made for centuries using traditional glass processing, the sol–gel process offers an elegant, more versatile alternative. Typically, the technique involves heating the gel in a reducing atmosphere. The host matrix may be an inorganic gel or an organic–inorganic hybrid.

In Inorganic Gels. Many metallic nanoparticles have been precipitated in sol–gel-derived matrices. For example, silica sol–gel films were prepared by dipping, starting from an acid-catalyzed solution of TEOS doped with Au, Ag, Pt, and Pd metal colloids. The temperature at which the metal particles precipitate by heating in air depends upon the metallic species: 200 °C for Au, 600 °C for Ag, 800 °C for Pt, and 1000 °C for Pd.[40] Silver metal nanoparticles were also produced in silica by introducing AgNO$_3$ in the sol–gel precursor solution. The silver ions were thermally reduced in air at 800 °C, giving an intense yellow coating film. The silver metal particles were observed by transmission electron microscopy and X-ray diffraction. The diameter of the silver particles was found to be about 10 nm. Thermochromic effects have been observed in such Ag colloid-doped gels.[41]

In Ormosils. Innocenzi and Kozuka made thin films of methyltriethoxysilane-derived gels containing Ag particles.[42] The average particle size was 10 nm. Ormosil matrices can also be doped with other metals, such as Au and Pt, as both bulk and thin-film forms. The main advantage of an Ormosil matrix is the ease of fabrication of large, crack-free samples. As in the case of the inorganic matrix, the metal clusters were incorporated into the Ormosil matrices by dissolving metal salts into the precursor solution prior to gelation. Reduction of the metal ions
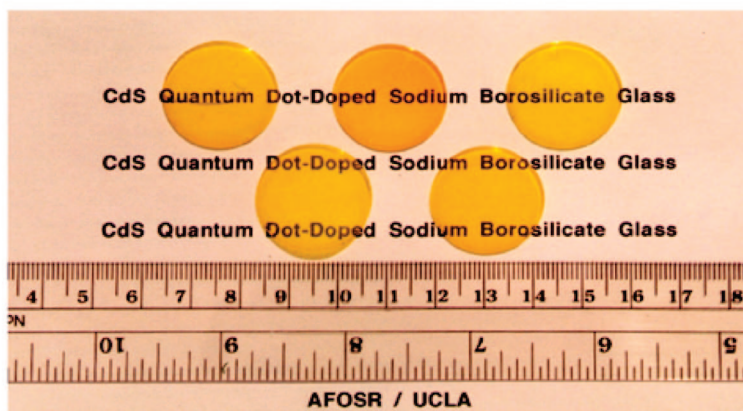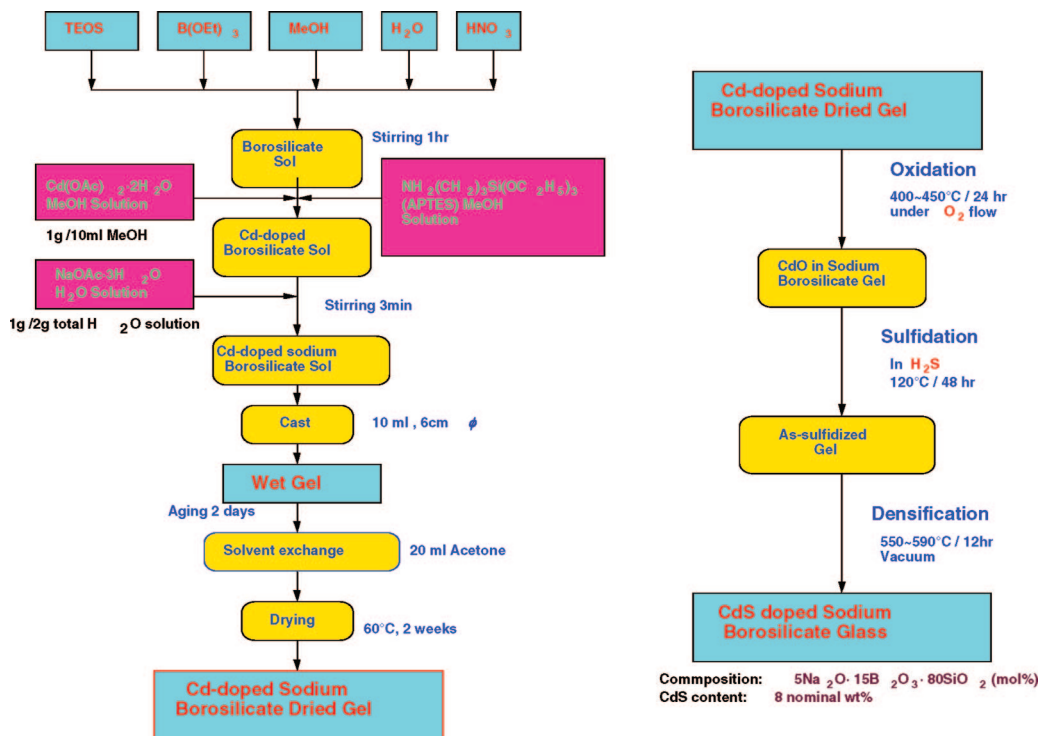
TEOS   B(OEt)$_3$ MeOH   H$_2$O   HNO$_3$

Borosilicate Sol — Stirring 1hr

Cd(OAc)$_2$·2H$_2$O MeOH Solution — 1g /10ml MeOH

NH$_2$(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$ (APTES) MeOH Solution

Cd-doped Borosilicate Sol

NaOAc·3H$_2$O H$_2$O Solution — 1g /2g total H$_2$O solution

Stirring 3min

Cd-doped sodium Borosilicate Sol

Cast — 10 ml , 6cm ϕ

Wet Gel — Aging 2 days

Solvent exchange — 20 ml Acetone

Drying — 60°C, 2 weeks

Cd-doped Sodium Borosilicate Dried Gel

Cd-doped Sodium Borosilicate Dried Gel

Oxidation — 400~450°C / 24 hr under O$_2$ flow

CdO in Sodium Borosilicate Gel

Sulfidation — In H$_2$S 120°C / 48 hr

As-sulfidized Gel

Densification — 550~590°C / 12hr Vacuum

CdS doped Sodium Borosilicate Glass

Compposition: 5Na$_2$O· 15B$_2$O$_3$· 80SiO$_2$ (mol%)
CdS content: 8 nominal wt%

CdS Quantum Dot-Doped Sodium Borosilicate Glass
CdS Quantum Dot-Doped Sodium Borosilicate Glass
CdS Quantum Dot-Doped Sodium Borosilicate Glass

AFOSR / UCLA

FIGURE 9. Processing route of CdS-doped borosilicate glass.

is not achieved at high-temperature reduction in such matrices. Instead, it was achieved through UV irradiation. The correlation between the resonance absorption position, particle size, and volume fraction of the colloidal metal particle was investigated and discussed. X-ray analysis showed the metal particles to be crystalline with a face-centered cubic (FCC) structure. The metal particle size and size distribution were studied by transmission electron microscopy.[43]

6. Colloidal Oxide Particles

Organic polymers tend to be soft and easily deformable, and in some cases, it is desirable to improve their mechanical properties. This can be done through the incorporation of oxide colloidal particles, which increase the elastic modulus of the polymeric matrix. Of particular interest is the reinforcement of siloxanes with silica colloidal particles. There are numerous publications and patents on these types of nanocomposites.[44,45] A signifi-

cant number of patents for such materials have been granted in the field of abrasion-resistant coatings on polymeric ophthalmic lenses. In some cases, the coatings are tintable and/or UV-curable.[46] Colloidal particles other than silica (TiO$_2$, ZrO$_2$, and Al$_2$O$_3$) have also been doped into siloxane matrices.[47] The presence of colloidal silica particles in gels also facilitates the deposition of thick coatings, up to 300 μm.[48] Colloids have been shown to limit the cracking observed during the drying phase of a SiO$_2$ gel synthesis. Large bulk pieces can be made.[49]

A more recent development in this area is the synthesis of core–shell structures, in which the core and shell of a nanoparticle consist of different materials. The core may be a semiconductor, and the shell may be a metal or vice versa. Alternatively, the core may be an oxide, a polymer, or a dye, and the shell may be a semiconductor, a polymer, a metal, etc. There are many possible ways of tailoring the structure of theses nanoparticles. Sol–gel processes are ideally suited for the synthesis of such
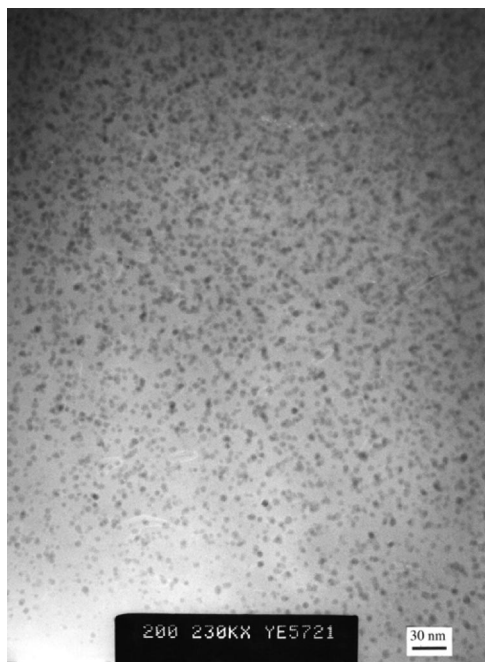
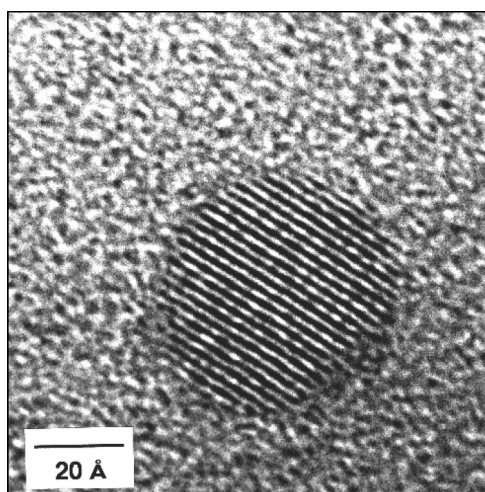**FIGURE 10.** CdS nanoparticles in borosilicate glass.

FIGURE 11. CdTe nanoparticle in a sol–gel-derived borosilicate matrix (5 wt % CdTe, at 500 °C/4 h).

architectures. For example, the particles can be prepared by reverse microemulsion methods. In some cases, a passivation layer, e.g., an aminosilane amorphous layer, is in contact with the core.[50] The optical properties of such core–shell structures are of great interest. For example, luminescent nanocrystals can find interesting applications as light-emitting transparent materials. Buisetter et al. describe the growth of lanthanide-doped vanadate and phosphate nanoparticles through colloidal synthesis, with average sizes smaller than 10 nm. Improvement of the luminescent properties of the nanocrystals is achieved through the elaboration of a core/shell nanostructure, obtained after the growth at the surface of an amorphous SiO_2 shell or a crystalline La phosphate shell.[51] $FeNi_3$/Al_2O_3 core–shell nanocomposites, where individual $FeNi_3$ nanoparticles are coated with a thin layer of Al_2O_3, were fabricated by a modified sol–gel method. The magnetic

properties of such nanostructures were also investigated.[52] Reactive core–shell nanoparticles have also been prepared using an amphiphilic organic polymer and a metal oxide precursor. The polymer-coated Al_2O_3 nanoparticles are thought to be formed by nucleation, with a core–shell structure forming later. Nanoparticles prepared using 10 wt % $Al(OiPr)_3$ yielded films that, depending upon the process conditions of the nanoparticles, possessed core–shell nanoparticles with a median diameter of 45 ± 2 nm and a T_g that was 27 °C above that of the matrix polymer.[53] Many other systems have been investigated. Surface-modified amorphous metal oxide nanoparticles of titanium, zirconium, tantalum, yttrium, and vanadium were synthesized using these novel precursors in a microemulsion-based sol–gel process. Particles with diameters below 200 nm were prepared.[54] This core–shell approach was also successful in the synthesis of new, complex semiconductor nanostructures. Colloidal CdSe/ZnS core–shell nanocrystals, with a narrow size distribution, were dispersed in a hybrid sol, resulting from the hydrolysis of TEOS and 3-glycidoxypropyltrimethoxysilane.[55] Finally, in a recent review, Burns et al.[56] reported that they have incorporated multiple tetramethylrhodamine isothiocyanate dye molecules into uniform, monodisperse, 25 nm diameter silica core–shell particles. They have observed significant enhancements in the brightness and stability of the organic dyes. They call these "nanobio" core–shell particles "C-dots". The core–shell interactions are thought to play a significant role in the enhancement of dye properties, perhaps through an increase in the dye rigidity. They also report many mechanisms by which these core–shell architectures can be designed for various "nanobio" applications. This is an exciting area of research that will probably yield many novel nanoarchitectures with heretofore unachievable properties.

Conclusion

In the design of complex nanoarchitectures, the main advantage of the sol–gel process is the versatility in the control of size, distribution, and arrangement of nanopores, for example through self-assembly. This nanoporosity can be functionalized using organic molecules or polymers as the gel developed or even after as the gel has dried. Furthermore, through careful heat treatment and dependent upon the chemistry of the starting solution and the thermal tretment, many kinds of nanoparticles (oxides, sulfides, metals, and semiconductors) can be grown within those nanopores, resulting in families of nanomaterials heretofore very difficult to fabricate. The versatility of the process is in large part due to the rich and varied chemistry of organometallic precursors, combined with the low processing temperature. As a result, the sol–gel process is likely to continue attracting the attention of chemists interested in designing advanced nanomaterials.

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