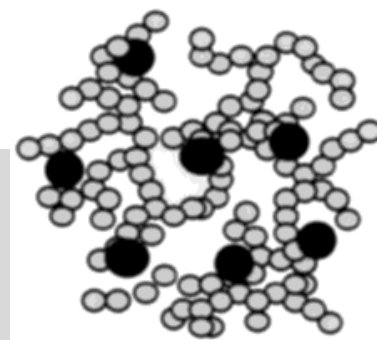


# Tailoring Advanced Nanoscale Materials Through Synthesis of Composite Aerogel Architectures\*\*

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and Debra R. Rolison\*

*Introducing a desired solid guest to an about-to-gel silica sol prevents complete encapsulation of the guest particles by the silica, such that the composite retains the bulk and surface properties of each component on the nanoscale. The transport- and density-dependent properties of the composite aerogel can be tuned by varying the volume fraction of the second solid, thereby increasing the design flexibility of these nanoscale materials for optical, chemical, thermal, magnetic, and electronic applications. The chemical and physical properties of the composite material can be further engineered at multiple points during sol-gel processing by modifying the host solid, the guest solid, the composite gel, or the composite aerogel.*



## 1. Introduction

Using silica sol as a glue, we have developed a general method to prepare composites of particulate guests and nanoscale silica that are highly porous, have high surface areas, and can be nanoscopically tailored to suit specific applications. The properties of the particulate guest are retained in the composite, thereby creating a composite that unites the continuous mesoporous network and high surface area of silica gel networks with pre-selected chemical, physical, and optical properties of the guest solid. The use of sol-gel chemistry to create these composites affords enormous flexibility to tailor them with solution- and gas-phase reagents at various stages of the wet gel preparation or after supercritically drying the wet gel to form the aerogel, as shown in Figure 1.

Sol-gels and sol-gel composites can be prepared with lower densities and higher porosities and surface areas than conventional ceramics, which confers on them novel physical and chemical properties.<sup>[1]</sup> Sol-gel-derived materials, as produced by the hydrolysis and condensation of metal alkoxide precursors ( $M(OR)_n$ ), Equations 1 and 2, respectively, as shown for generation of silica from a tetraalkoxysilane precursor, have been widely studied for applications requiring

specialty optical, thermal, and/or electronic nanoscale materials.<sup>[2]</sup>

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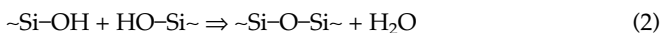
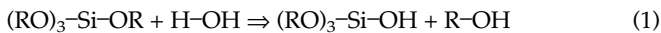
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Catalytic, electrocatalytic, and sensing applications, in particular, are facilitated by high active surface areas contained within a highly porous medium so that rapid reactant/analyte throughput to the active sites occurs. The use of supercritical-fluid drying techniques to produce an aerogel from

a wet gel affords a significant improvement in the surface area and porosity of the dried material,<sup>[1,3]</sup> as contrasted with conventional ambient-drying techniques that yield a xerogel, as illustrated in Figure 2. Aerogels are highly porous solids (75–99% open space) that contain mesopores (pores 2–50 nm in size) and micropores (pores <2 nm) and express high surface areas (up to 1000 m<sup>2</sup>/g) and ultra-low densities (down to 0.003 g/cm<sup>3</sup>).<sup>[2a,4]</sup> These physical attributes are also present in composite aerogels prepared from wet composite gels.



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*Debra Rolison (Ph.D., 1980, University of North Carolina at Chapel Hill) currently heads the Advanced Electrochemical Materials section. Her program focuses on the influence of nanoscale domains on electron- and charge-transfer reactions and the design and synthesis of new nanostructured materials and composites for catalytic chemistries, energy storage and conversion (fuel cells, supercapacitors, batteries, thermoelectric devices), and sensors. Dr. Rolison was a member of the Advisory Board for Analytical Chemistry and is a current member of the Editorial Boards of the Journal of Electroanalytical Chemistry and Langmuir. She is a member of the Board of Directors for the Society for Electroanalytical Chemistry and has served since 1997 as editor of the society's newsletter: SEAC Communications.*

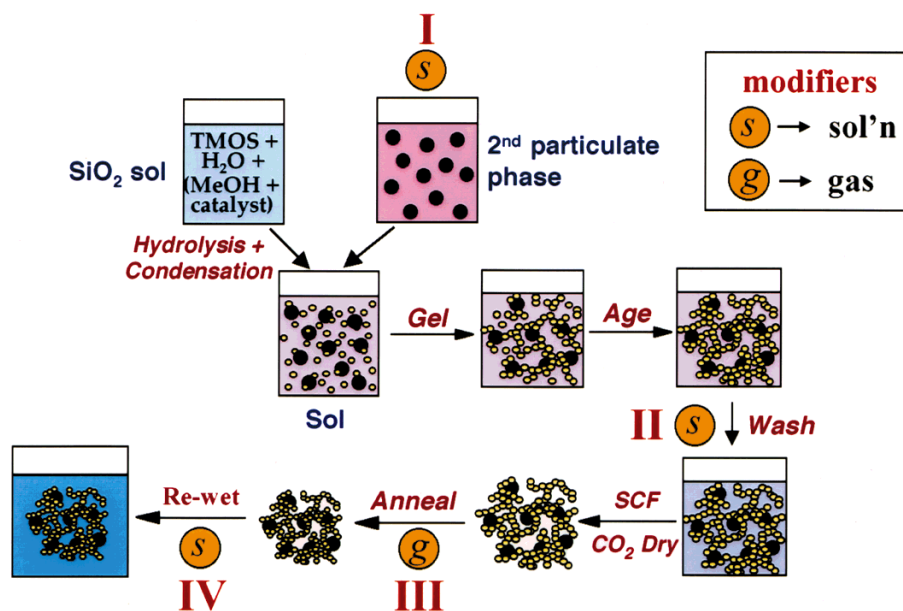


Fig. 1. A schematic detailing how the sol-gel process is used to prepare composite gels and aerogels. The required properties of the composite material can be selected prior to gelation of the  $\text{SiO}_2$  sol on the basis of which particulate guest is chosen. Additional opportunities exist to nano-engineer the properties of the composite gel and/or aerogel with solution- or gas-phase modifiers, as indicated at points I, II, III, and IV. TMOS = tetramethoxysilane. SCF = supercritical fluid. SCF  $\text{CO}_2$  drying conditions:  $T_c = 31^\circ\text{C}$ ,  $P_c = 7.4\text{ MPa}$ .

sional network, and ii) guest-host materials, in which the wet sol-gel or dried gel serves as a host matrix for particulate or molecular solids.

We use silica sol as a nanogluue to prepare composite aerogels by dispersing a non-bonding solid (either in colloidal or non-colloidal form) in an about-to-gel silica sol.<sup>[9-11]</sup> By minimizing the time for interaction between the sol and particulate prior to gelation, it is possible to avoid encapsulation of the guest by the silica host. However, the guest solid, even when small enough to move through the mesopores of the gel, is sufficiently incorporated into the three-dimensional silica network that it does not elute out either upon replacing the pore-filling liquid or during supercritical drying. The particulate is therefore thoroughly immobilized, yet readily accessible via the mesoporous network.

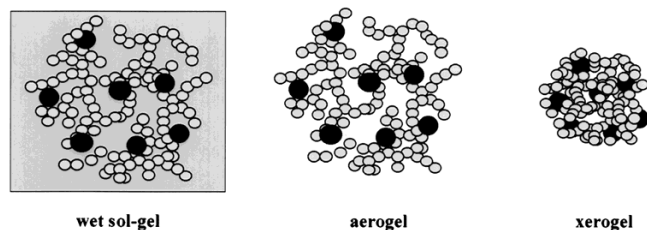


Fig. 2. Representations illustrating the difference in the degree of shrinkage experienced by a composite gel dried by supercritical-fluid extraction (to produce an aerogel) or by ambient evaporation of the pore-filling liquid (to produce a xerogel). The composite gel that is dried to form an aerogel is characterized by greater porosity and decreased encapsulation of immobilized guest particles than when dried to form a xerogel.

Silica gels (composed of  $\sim 10\text{ nm}$   $\text{SiO}_2$  particles<sup>[5]</sup>) and composite gels have been widely studied, along with synthetic methods that retain the desired property of the guest phase.<sup>[6,7]</sup> Due to the mild conditions employed during sol-gel processing, temperature-sensitive moieties (such as molecules and biomolecules) can be incorporated as guests. Ambient processing also compatibly integrates sol-gels, which are readily fashioned in assorted physical forms (e.g., thin film, monolith, powder), with other materials to form multilayer or composite structures.<sup>[2]</sup>

Sol-gel-derived hosts containing highly dispersed particulate guests have previously been studied for their optical non-linearity, catalytic, biocatalytic, electrocatalytic, and sensing capabilities.<sup>[7,8]</sup> These nanocomposites fall into two general categories: i) hybrid systems, in which a metal alkoxide and a particulate precursor that contains alkoxide functionalities are reacted together to produce a single-phase, three-dimen-

## 2. Alternate Approaches to Fabricate Guest-Host Silica Composites

Our approach is distinct from previous approaches in which the guest solid is covalently linked to the three-dimensional silica network during gelation.<sup>[12]</sup> Covalent attachment of the guest is achieved either by mixing it with the sol-gel precursors prior to gelation (to form a single hetero-network)<sup>[12,13]</sup> or by infiltration of the guest after gelation followed by covalent bonding to the surfaces of the wet gel.<sup>[13f]</sup> These methods are restricted to molecules and particulates for which (often complex) synthetic routes can be found to attach a functional group that covalently bonds to the silanols ( $\text{Si-OH}$ ) of the silica network.

Our method also differs from impregnation techniques that produce guest-host nanocomposites. Using these approaches, reactive precursors are infused into a pre-formed silica or other mesoporous network and reacted to form a second particulate phase dispersed through the host.<sup>[6,7,12c,14]</sup> The chemical composition and physical form of the impregnated phase are determined by precursor chemistry and concentration, reaction conditions (e.g., temperature, means of mass transport of the reactants), and post-treatment of the composite. Impregnation techniques are often plagued by dispersions in final particle sizes and non-uniform particle distribution through the silica matrix.

Our method is unique in that the guest associates with the silica sol (host) for just seconds to a few minutes (rather than hours) before gelation occurs. Earlier work on guest-host nanocomposites, including aerogel-based composites,

have involved extensive physical mixing of the solid with either the sol-gel precursors or sol to prevent settling of the solid prior to gelation.<sup>[13g,15]</sup> Fricke and co-workers first demonstrated this concept in their investigations of silica aerogels containing carbon (an opacifier) for thermal insulation.<sup>[15b]</sup> Their subsequent work has shown that colloidal ZnO-silica aerogel nanocomposites retain the characteristic yellow-green photoluminescence of ZnO nanocrystals (also illustrated by Deng, et al., for ZnO-silica composites containing ZnO made by reacting Zn salts introduced by impregnation<sup>[16]</sup>).

Although certain properties are independent of mixing times, we find that extensive mixing of the particulate guest with the silica sol prior to gelation can lead to the loss of critical properties for some materials, particularly transport properties (which require intimate contact between guest particles) and chemical properties (which involve guest interaction with molecules in the mesopores). For instance, when we prepared carbon-silica composite gels using prolonged mixing times to ensure thorough homogenization of the carbon and silica phases, electronic transport paths through the carbon were disrupted in the dried composite.<sup>[9]</sup> Minimizing the interaction time between the same ratios of carbon to silica, however, yields a composite in which the carbon is uniformly dispersed, yet electrically conducting. We expect the desirable physical, transport, and chemical properties of other solids to be expressed in the composite when we limit exposure of the guest to the silica sol.

Applications in which gas- and liquid-phase immersion is employed (i.e., catalysis) may require gels with high mechanical and thermal durability.<sup>[17-19]</sup> We find that the presence of the particulate guest often strengthens the nanoglued composite aerogel relative to the mechanical durability of pure silica aerogel, even without thermally densifying<sup>[16b]</sup> the composite.

### 3. Chemical and Physical Diversity of Composite Aerogels

We have demonstrated immense range in the size and composition of the guest solid in silica-based composite aerogels, as seen in Figure 3. Guests whose sizes span over five orders of magnitude (from several nanometers to sub-millimeter) and whose chemical compositions vary from colloidal metal to metal oxides, non-oxide semiconductors, carbon blacks, and polymer particles have been immobilized in the silica matrix. In general, the known attributes of the guest, as well as the structure of the silica network (Fig. 4), are retained in the composite gel or aerogel.<sup>[9,11]</sup> The composite chemical, optical and/or electrical properties can therefore be predetermined to suit the desired application.

Particulate-silica composite aerogels are especially suited for technologies that require highly dispersed, readily accessible reactive sites (e.g., catalysts, sensors). The total pore volumes and Brunauer-Emmett-Teller (BET) surface areas of the

silica-based composite aerogels shown in Figure 3 are intermediate to the values for the silica and guest particulate. Pure silica aerogel (~1 % dense) has a pore volume of ~4.4 cm<sup>3</sup>/g; silica-based composite aerogels still preserve pore volumes characteristic of highly mesoporous materials. The density-



Fig. 3. Silica-based composite aerogels (from left to right): pure silica aerogel [overlying Ti-V/Zr-Nb/Hf-Ta in the periodic table]; colloidal Pt-silica composite aerogel (2 nm Pt sol); colloidal Au-silica composite aerogel (30 nm Au sol); carbon black-silica aerogel (Vulcan carbon black, XC-72); poly(methylmethacrylate)-silica composite aerogel (polymer  $M_w \sim 15,000$ , sieved to  $<44 \mu\text{m}$ );  $\text{Fe}^{\text{I}}(\text{bpy})_3\text{NaY}$  zeolite-silica composite aerogel (0.1–1  $\mu\text{m}$  type Y zeolite crystallites modified with iron(i)tris-bipyridine); titania (aerogel)-silica composite aerogel ( $\mu\text{m}$ -sized particulates composed of ~15 nm  $\text{TiO}_2$  aerogel domains); and titania-silica composite aerogel (20–40 nm Degussa P-25  $\text{TiO}_2$ ). All samples shown are ~1 cm diameter monoliths of varying lengths.

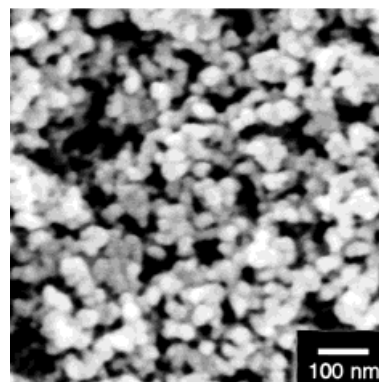
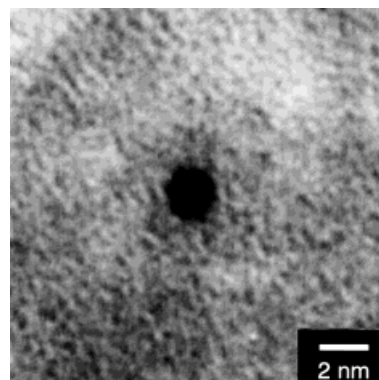


Fig. 4. (bottom) SEM of a colloidal Pt-silica composite aerogel. The silica particles appear gray and the mesopores are black. The beaded-necklace morphology is characteristic of the fractal structure of base-catalyzed silica aerogel [5]. The guest, ~2 nm Pt particles, is obscured by the surrounding silica host. (top) HRTEM of a colloidal Pt-silica composite aerogel. The mottled gray region is the amorphous silica host, which encases the 1.8 nm Pt particle. HRTEM studies of composites containing 5 nm or larger gold particles indicate that the nanoparticle surface is partially exposed to the mesoporous network, in agreement with the finding that colloidal gold guests sized at ~5 nm cannot be chemically modified.

and transport-controlled properties of composite aerogels can also be tailored by adjusting the mass or volume ratio of silica sol-to-guest particulate. For example, the density of zeolite-silica composite aerogel reflects a weighting of the densities of the individual components (silica aerogel and zeolite powder).<sup>[9]</sup>

The optical properties of composite gels and aerogels generally reflect those of the guest because base-catalyzed silica aerogels are transparent and featureless over most of the UV-visible<sup>[11]</sup> and infrared (IR)<sup>[9]</sup> spectral regions. The range of optically active guests includes even organic species given the gentle processing conditions and known tolerance of organic molecules to supercritical CO<sub>2</sub>.<sup>[20]</sup> Composite gels and aerogels are readily characterized by optical spectroscopies: for example, Fe<sup>II</sup>(bpy)<sub>3</sub>NaY zeolite-silica and poly(methylmethacrylate)-silica composite aerogels exhibit the infrared absorption features characteristic of the bipyridine and methylmethacrylate moieties, respectively.<sup>[9]</sup>

The innate optical character of commercially relevant metal oxide guests, such as photocatalytic titania, is also preserved in the metal oxide-silica composite aerogel. Opaque titania (Degussa) when incorporated into a composite yields an aerogel that exhibits a broad UV absorbance characteristic of the large bandgap semiconducting guest. Titania (aerogel)-silica composite aerogels (see Fig. 3) have a UV absorbance characteristic of pure titania aerogel, which is translucent and exhibits a spectrum more molecular in nature.<sup>[9]</sup> The improved photocatalytic activity of titania aerogel relative to more conventional forms has already been noted,<sup>[21]</sup> but titania aerogels are difficult to prepare as crack-free monoliths or films.<sup>[22]</sup> The transparency of silica aerogel permits effective illumination of the titania component in the composite aerogel, and may improve practical photocatalysts by permitting efficient illumination of the entire photoactive material within a structure that facilitates reagent flux to (and from) the active sites through the continuous mesoporous network.

Colloidal gold-silica composite gels and aerogels retain the color and transparency of the native metal sol (see Fig. 3),<sup>[9,11,23]</sup> because the characteristic plasmon resonance at 500–550 nm of the nanoscale gold particles is unobscured by the transparent silica matrix. The plasmon resonance peak position is identical for the Au sol and the colloidal Au-silica composite gel, both of which surround the colloidal gold with a condensed fluid. The plasmon resonance peak is blue-shifted (relative to the sol) in the composite gold-silica aerogel, in which the gold particles are now surrounded by a mixture of more air than silica. The blue-shift is in keeping with the relationship between maximum absorbance and solvent refractive index in the Mie approximation for colloidal metal particles.<sup>[11]</sup>

The retention of the metal particle's size and its optical properties in our colloidal gold-silica composite gels and aerogels distinguishes them from compositionally related composites in which the gold particles are covalently attached to the silica network or are stabilized by surfactants during gelation. Gold-silica core-shell particles exhibit a red-

shifted Au plasmon resonance,<sup>[8f,g]</sup> as do gold-silica composites derived from organically modified sol-gel monomers that are used to stabilize the dispersed Au particles.<sup>[8b,12a,c]</sup> Composites in which the metal particle size evolves over time, as occurs in the surfactant-mediated synthesis of gold-silica gels from gold-containing micelles, also exhibit a red shift relative to the Au sol.<sup>[15c]</sup>

## 4. Designer Architectures

Particulate-silica composite aerogels are platforms that provide opportunities to engineer a broad range of nanoscopic materials with specific pre-selected properties. The gel preparation scheme, Figure 1, offers multiple means to further tailor the optical, chemical, and physical properties of the host solid, the guest solid, the composite wet gel or the dried aerogel via solution- or gas-phase modification.

Additional tailoring of the composite gel architecture can be achieved by modifying the surface of the particulate guest prior to gelation, as shown in Figure 1I. We have demonstrated that active sites that are introduced to the surface of the guest particles prior to gelation remain accessible to external reagents after supercritical drying. Carbon-supported metal colloids in carbon-silica composite aerogels (produced by combining colloidal metal-modified Vulcan carbon with silica sol) remain accessible to CO and MeOH, and have been electronically addressed within the aerogel to catalyze redox reactions.<sup>[24]</sup>

High-surface-area carbon blacks are typically used in fuel cells to disperse the nanoscale electrocatalyst<sup>[25]</sup> and then fabricated into a fuel-cell electrode of the required geometry by combining with a porous binder, such as poly(tetrafluoroethylene). Composite aerogels should improve existing electrocatalytic technologies because their integrated structure offers multifunctionality by providing superior access of fuel and oxidant to the dispersed, carbon-supported catalyst via the continuous mesoporous network, while also maintaining electronic conductivity throughout the composite.

Modified carbon-silica composite aerogels are potential black optical materials as well. Neither ambient nor He-Ne laser light is transmitted through a 1 cm monolithic carbon-silica composite aerogel, despite its high porosity (Fig. 5).<sup>[9]</sup> In contrast, native silica exhibits clarity that transmits light with little scattering (see Fig. 3). Opaque or low-reflectivity coatings and monoliths may be prepared and the wavelengths that are absorbed can then be extended beyond the visible by adsorbing molecular modifiers to the carbon.

The surface of the guest particulate may also be tailored following gelation by adding solution-phase reagents to the pore-fluid washes that are performed prior to supercritical-fluid drying, as shown in Figure 1II. For example, the surface of gold colloids larger than ~20 nm remains accessible to external reagents via the three-dimensional mesoporous network of the composite gel.<sup>[11]</sup> The base-conjugate form of the pH-sensitive dye methyl orange preferentially adsorbs (from

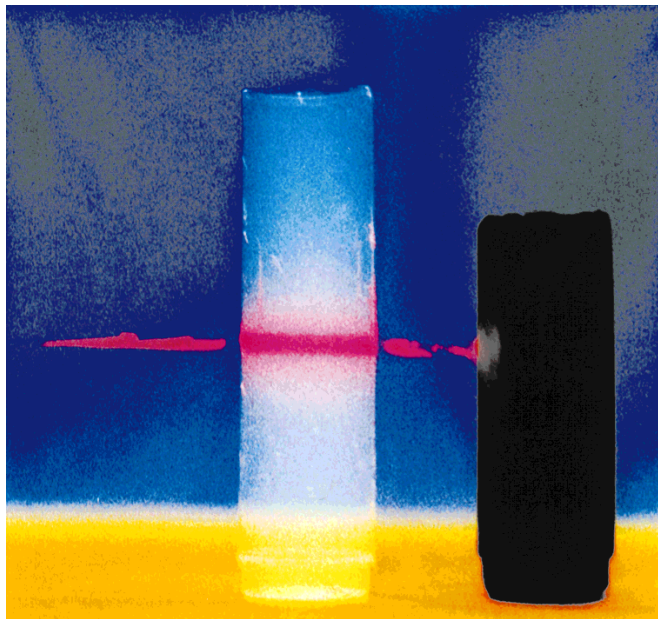


Fig. 5. He-Ne laser (from left) irradiating air, SiO<sub>2</sub> aerogel, and Vulcan carbon-silica composite aerogel. No light is transmitted through the carbon-silica composite aerogel, even though it is 80 % open space.

acetone solution) to the metal surface in colloidal Au-silica composite wet gels, and not to the surface of the silica domains. The UV-visible absorption spectrum of a methyl-orange-modified colloidal Au-silica gel exhibits resolved peaks for colloidal Au and methyl orange.<sup>[11]</sup> A more complex modification of the metal surface architecture using solution-phase reagents can be conceived that customizes these composites with molecular recognition centers for analyte specificity or tailors the colloidal metal-modified carbon-silica composites for more efficient electrocatalysis.

Modification of the composite aerogel following supercritical drying (Fig. 1III and 1IV) may also be employed. For composite aerogels that do not contain organic moieties, partial densification at elevated temperatures can be used to strengthen the silica network.<sup>[15,26,27]</sup> Silica or colloidal Au-silica composite aerogels heated to 900 °C shrink (~50 % reduction in the size of the monolith), but the primary loss in free volume, as determined by N<sub>2</sub>-physisorption measurements, occurs by collapse of the micropores (pores <2 nm), while most of the mesoporosity (2–50 nm pores) is preserved (Fig. 6). Preserving the mesoporous free volume means that the most facile mass-transport pathways through the composite aerogel for gas- or solution-phase reactants remain unaltered. Furthermore, the composite constitutes a rigid solid architecture, such that the silica aerogel structure and metal particle size distribution are retained in partially densified colloidal Au-silica composite aerogels.<sup>[23]</sup>

Partially densified composite aerogels are sufficiently durable that they remain intact upon reimmersion into liquids (Fig. 1IV).<sup>[17b,23,25]</sup> We have demonstrated this durability by preferentially adsorbing methyl orange from solution onto the Au surface in partially densified colloidal Au-silica com-

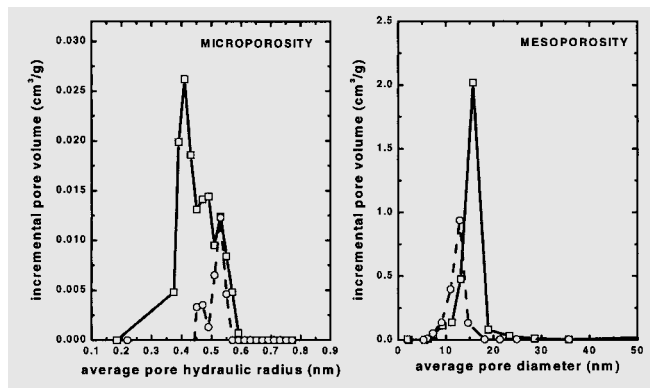


Fig. 6. Micropore and mesopore size distributions for silica aerogel annealed at 500 °C [—□—] (minimally shrunk compared with as-supercritically dried aerogel) and densified at 900 °C [—○—] to ca. 50 % of its original size. Loss of both meso- and microporosity is observed, but direct analysis of the total pore volumes in each of these regions indicates a 40 % loss of mesoporous volume and a >85 % loss of microporous volume upon partial densification.

posite aerogels,<sup>[9,23]</sup> analogously to the specific adsorption of the dye in colloidal Au-silica composite wet gels, as described above.<sup>[11]</sup> This surface-specific modification is consistent with the retention of a continuous mesoporous network in silica-based composite aerogels, even after partial densification, as indicated by our N<sub>2</sub>-physisorption studies comparing as-prepared and partially densified aerogels (see Fig. 6). On the basis of these independent measurements of the total sample pore volume that is contributed by micro- and mesopores, nearly 60 % of the 500 °C-annealed aerogel mesoporosity is preserved in the 900 °C-partially densified aerogel, while <15 % of the microporous volume is retained in the partially densified sample.

We have also verified the feasibility of optical or colorimetric sensing with composite gels by using a combination of the modification steps illustrated in Figure 1. We demonstrated this multistep modification strategy by thermally densifying 50 nm colloidal gold-silica composite aerogels and modifying the colloidal Au guests with methyl orange by immersion of the partially densified composite aerogel into a non-aqueous solution of the dye (Fig. 1IV).<sup>[9,11,23]</sup> Analogously to the wet composite gels discussed above, resolved peaks for the Au plasmon resonance and the methyl orange (base-conjugate form) absorbance are seen in the UV-visible spectrum of a methyl-orange-modified colloidal gold-silica composite aerogel that was thoroughly rinsed with acetone, then air-dried.<sup>[9,23]</sup> Exposing the dye-modified, air-dried composite to HCl vapor (i.e., Fig. 1III), produces a red-shift in the dye's absorption, corresponding to its protonation.

The gas-phase acid molecules may be detected either visually or by instrumental colorimetry. Visual detection is possible because although the surface coverage of the adsorbed dye is quite low (typically <0.1 of a monolayer), the surface-to-volume ratio of the composite is enormous, which brings the effective concentration of the dye in the modified composite aerogel to millimolar levels. Color changes are rapid, be-

cause of the high porosity, and are readily discerned by eye. Upon uptake of methyl orange, the color of the colloidal Au-silica composite aerogel changes from cranberry to peach (again, no methyl orange is retained in partially densified pure silica), and a further color change from peach to bright pink occurs within seconds of exposure of the dye-modified Au-silica composite aerogel to HCl vapor.

## 5. Methods

### 5.1. Preparation of Composite Aerogels

Our recipes for base- and acid-catalyzed gels are based on published procedures,<sup>[10]</sup> and are described elsewhere in detail.<sup>[11]</sup> Equal volume percents of particle suspensions (Au or Pt sol) and silica sol were combined, the mixture stirred for 1 min, and then poured into molds (and sealed with Parafilm) prior to gelation. Volume percents ranging from 1–90 vol.-% solid were incorporated into particulate-silica composites. For guests at <50 vol.-%, the solid was rapidly added to the silica sol with stirring, mixed for 15 s, and the dispersion was then poured into molds seconds before gelation. For >50 vol.-% solid, a homogenous dispersion of the solid in the gel is achieved by combining the silica sol and solid in a vial, which is then sealed and vigorously shaken until gelation occurs. Ultrasonication was also attempted, but some solids (i.e., carbons and polymers) phase-separate from the silica sol during sonication. The gelation time is determined by the type and amount of catalyst used, and in some cases on the solid incorporated [in general, for a 15-ml total volume of silica sol: 0.7 ml of 30 % NH<sub>4</sub>OH (base-catalyzed gels) rendered a gelation time of ~1.5 min; 0.07 g of HCl (acid-catalyzed gels) yielded ~3 min gelation times]. One solid, titania aerogel, decreased the gelation time compared to neat silica sol, proportionate to the amount of solid added. The composite gels were aged for 10–20 min, then rinsing was initiated.

### 5.2. Physical Characterization

Samples were analyzed using a Leo 1550 scanning electron microscope (SEM) and a Hitachi H-9000 high-resolution transmission electron microscope (HRTEM). The SEM samples were prepared by cleaving and sputter coating with <5 nm Pd-Au, and the extraction voltage was kept to 3–5 kV to minimize charging effects. Edge-mounted slices from the monolith or powdered samples supported on holey-Al grids were used for HRTEM. N<sub>2</sub>-physisorption measurements were performed on a Micromeritics ASAP 2010 accelerated surface area and porosimetry system, with reported pore size distributions derived from programs included in the instrument software.

## 6. Conclusions

Using silica sol as a nanoglue, we have demonstrated broad flexibility in the design of nanocomposite materials for

a diverse range of applications. Because composite gels and aerogels prepared using silica nanoglue retain the surface and bulk properties of each component, improvements to current technologies may be readily achieved using existing materials. The ability to form an interconnected network of the secondary or guest phase allows for ionic, electronic, and thermal transport properties not attainable in a silica system.

Composite aerogels are customizable platforms around which advanced structural and chemical architectures may now be designed. Not only is the range of guest particulates virtually limitless, but any primary guest phase can potentially be modified prior to incorporation. For example, we are expanding this method to include other nanoscale materials, such as thiolated Au colloids that possess specific active functionalities (e.g., photo- or electroactive molecules). In addition, either the particulate guest or silica host may be tailored for a specific application by reaction at, or molecular adsorption to, their surfaces, which remain accessible to external reagents via the continuous mesoporous network of the composite aerogel.

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