Silica Sol as a Nanoglue: Flexible Synthesis of Composite Aerogels

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Low-density nanoscale mesoporous composites may be readily synthesized by adding a colloidal or dispersed solid to an about-to-gel silica sol. The silica sol can "glue" a range of chemically and physically diverse particles into the three-dimensional silica network formed upon gelation. If the composite gel is supercritically dried so as to maintain the high porosity of the wet gel, a composite aerogel is formed in which the nanoscopic surface and bulk properties of each component are retained in the solid composite. The volume fraction of the second solid can be varied above or below a percolation threshold to tune the transport properties of the composite aerogel and thereby design nanoscale materials for chemical, electronic, and optical applications.

We used silica sol (where sol is a colloidal solid dispersed in a liquid) as a nanoscale glue to prepare composite gels and, ultimately, composite aerogels by dispersing a colloidal or noncolloidal solid of interest in an about-to-gel silica sol (1-3). As the colloidal silica gels through condensation chemistry (4), it incorporates all of the dispersed second phase into its three-dimensional (3D) network. After gelation, neither repeated washings (to replace the pore-filling liquid) nor supercritical drying [to create an aerogel (4, 5)] will flush the immobilized particles out of the silica structure—even particles as small as 2 nm are retained in the gel (1, 6, 7).

Waiting until the silica sol is just about to gel before introducing the second solid phase creates a composite network that is distinct from previous approaches to prepare nanocomposite gels. Prior work includes (i) hybrid composites, in which the second component is introduced either at the silicon precursor stage or well before gelation occurs (8); (ii) composites formed by impregnating precursors into the silica network, which are then reacted to form a second phase in the solid silica structure (9, 10); and (iii) composites in which the silica is used solely as a template for the formation of crystals or novel structures such as carbon nanotubes (11).

Our approach commingles the guest and silica sol (host) for only minutes, rather than hours, before gelation of the silica sol occurs. Minimizing the interaction time between the silica colloids and the guest [both before gelation and during aging (2)] prevents total encapsulation of the guest by the silica. For example, we found that extended mixing of guest and silica sol can interrupt transport paths in the second phase. Enormous flexibility in the choice of both the guest's composition and size is possible, as shown in Fig. 1, where the second solid phase can be any of a number of functional materials [including colloidal metals (12-14), metal oxide (15-17) and zeolite particles (18, 19), carbon blacks, and polymer particles] and can range in size from a few nanometers to tens of micrometers.

Depending on the chosen application, the optical, chemical, or electrical properties of the nanoscale mesoporous composite may be predetermined. In general, the known properties of the solid guest before incorporation into the aerogel are comparable to its properties in the composite gel or aerogel. Optical characterization is easiest for the composites that retain the optical transparency of pure silica aerogel, such as for immobilized metal colloids (Fig. 1), but even opaque composite

Fig. 1. Silica-based composite aerogels (from left to right): pure silica aerogel; colloidal Ptsilica composite aerogel (2to 3-nm Pt sol); colloidal Ausilica composite aerogel (30nm Au sol); carbon black-silica aerogel (Vulcan carbon black, XC-72); Fe^{II}(bpy)₃NaY zeolite-silica composite aerogel (0.1- to 1-µm zeolite crystallites); titania (aerogel)-silica composite aerogel (micrometer-size particulates composed



aerogels retain high porosity (Table 1), thereby ensuring access by external gas- and liquid-phase reagents to the interior of the composite aerogel for molecular recognition, sensing, or reaction.

Metal particles immobilized in xerogel and aerogel matrices have been evaluated for use as nonlinear optical (20), catalytic and electrocatalytic (21), and sensor materials (22). In most cases, the metal particles are formed in situ from reactive precursors, and the processing conditions affect the size of the metal particles. Colloidal metal-silica aerogel composites (Figs. 1 and 2) allow the size of the immobilized metal particles to be determined before gelation, whereas the mild processing conditions permit the use of metal colloids that have been surface-modified with temperature-sensitive elements (such as organic dyes or biomolecules).

The optical character of a colloidal metalsilica composite aerogel can be monitored for colloidal metals modified with molecular tags. The visible absorption of colloidal Ausilica composite aerogels arises from the surface plasmon resonance of the colloidal Au (1). After adsorption of methyl orange dye to the surface of the aerogel-immobilized Au colloids, the spectral signature of the composite aerogel reflects the visible absorbance of the dye (in its base conjugate form) (Fig. 3). Methyl orange adsorbs selectively to the Au particles, because a pure silica aerogel does not retain the dye. The accessibility of the dye molecules within the aerogel monolith to reactant molecules can be demonstrated by exposing the methyl orange-modified Au-silica composite aerogel to vapor-phase HCl-as seen in Fig. 3, the visible absorbance shifts to one characteristic of the protonated dye (23, 24). Because of the high porosity of the composite aerogel, the protonation of the dye is complete in seconds.

Other solids are also readily incorporated into composite aerogels. Titania, a wide bandgap semiconductor, photocatalyzes mineralization of organic pollutants (25, 26). Its activity is determined by the amount of crystalline anatase

of ~15-nm TiO₂ aerogel domains); titania-silica composite aerogel (20- to 40-nm Degussa P-25 TiO₂); and poly(methylmethacrylate)-silica composite aerogel (polymer $M_{\rm w} \approx 15,000$, sieved to <44 μ m). See Table 1 for physical data on these types of composite aerogels. Photographed by N. Leventis (University of Missouri–Rolla) using a 50-mm macro lens.

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present and the number of surface –OH groups available for reaction [the latter of which correlates with surface area (25)]. Titania aerogels are noted for their mechanical fragility (27), but composite aerogels containing titania [preformed as either ultralow-density aerogel or a dense colloid (Degussa P-25, Degussa AG, Frankfurt, Germany)] can be fabricated as crack-free monoliths using silica sol as a nanoglue (Fig. 1) (28).

Efficient illumination of the aerogel-incorporated titania is feasible, because the silica aerogel is transparent and featureless throughout most of the ultraviolet-visible (UV-vis) region (Fig. 4). The UV-vis spectra for titania-silica composite aerogels reflect the absorption/scattering features of the titania guest so that titania (aerogel)-silica composite aerogels retain transparency, whereas titania (Degussa)-silica composite aerogels are highly absorbing and scattering (Fig. 1) (29). The titania (aerogel)-silica composite aerogel retains the continuous mesoporous structure of the silica aerogel (as weighted by incorporating the lower surface area titania aerogel) (Table 1), which allows ready molecular access to the nanoscopic titania photocatalyst inside the monolith.

Catalyst particulate—silica composite aerogels inherently form a "reactor," as seen for the titania-silica composite aerogel, and should offer an architectural way to bypass some masstransport limitations. For example, zeolites particularly those that are catalyst-modified are exemplary heterogeneous catalysts, but the native form of crystalline zeolite (~1-µm pow-

der) is too fine for practical use in fluidized beds, stationary beds, or continuously stirred tank reactors. Zeolites that are used in industrial reactors are mixed with aluminosilicate clavs and extruded into beads or pellets (30). The clay and zeolite particles form a composite structure that offers physical ruggedness under reaction conditions, but the clav hinders mass transport of reactants to the zeolite catalyst. Because of the continuous mesoporous network within the composite aerogel reactor, gas- or liquid-phase molecular reactants can rapidly enter the structure and react with the guest or catalyst, thus bypassing the mass-transport barriers imposed by amorphous clay binders. This approach can be generalized for particulate catalysts, oxide-supported catalysts, or polymers other than zeolites or photocatalysts.

The infrared signatures of Fe^{II}(bpy)₃modified NaY zeolite (Na+-compensated type-Y faujasite) or poly(methylmethacrylate) are retained in their respective composite aerogels (31, 32). These monolithic structures again maintain the meso- and microporosity of their respective components. The multipoint Brunauer-Emmett-Teller (BET) surface area of Fe¹¹(bpy), NaY-silica composite aerogel reflects a compromise between the surface areas of its silica and Fe^{II}(bpy)₃NaY components (Table 1). A significant increase in envelope density is observed for Fe^{II}(bpy), NaY-silica aerogel despite the low fraction of Fe^{II}(bpy)₃NaY zeolite incorporated in this composite (~ 2 wt %), so it is expected that density-based properties of the composite can be controlled by the relative ratios of the components.

Composite aerogels may also be used to design integrated electrocatalysts that contain a monolithic mesoporous structure and an electron conduction path. Fuel-cell electrocatalysts are typically supported on highly conductive, large surface-area carbon blacks to increase efficiency and reduce costs (33, 34). Carbon-silica composite aerogels may further improve this technology by dispersing and anchoring the carbon-supported electrocatalyst within the highly porous silica matrix, thereby facilitating access of reagents to the electrocatalyst and increasing the effective area of carbon/electrocatalyst available for redox reactions. In order for the composite aerogel to exhibit the necessary conductivity in



 Table 1. Summary of physical data for particulate guest and guest-silica composite aerogels. NA, not applicable; ND, not determined.

| Material | Weight (volume) fraction of guest (%) | Pore volume (ml/g) | BET surface area (m²/g) | Envelope density (g/cm³) |
|--------------------------------------------|---------------------------------------------|--------------------------|----------------------------------|--------------------------------|
| Silica aerogel | NA | 4.44 | 824 | 0.142 |
| Titania aerogel | NA | 0.35 | 137 | ND |
| Titania (aerogel)-silica composite | 10.9 (35.0) | 1.55 | 668 | ND |
| Titania (Degussa)-silica composite | 5.8 (35.0) | 1.42 | 383 | ND |
| Fe"(bpy) ₃ NaY zeolite | NA | 0.04 | 222 | 3.51 |
| Fe"(bpy) ₃ NaY-silica composite | 2.1 (5.5) | 2.32 | 732 | 0.382 |
| Vulcan carbon | NA | 0.83 | 232 | ND |
| Vulcan carbon-silica composite | 2.8 (10.7) | 1.55 | 731 | ND |

Fig. 2. Transmission electron micrographs of colloidal Au-silica composite aerogels showing Au colloids dispersed throughout the amorphous silica aerogel (left) and associated with the colloidal silica (right).



Fig. 3. The UV-vis absorption spectra of methyl orange in acetone (below its pK_a and after partial protonation with HCl) and after adsorption of the dye onto Au in colloidal Au-silica composite aerogels. The middle curve shows the surface plasmon resonance obtained for 50-nm colloidal Au in a Au-silica composite aerogel. Methyl orange is red at a $pH \approx 3.2$ and yellow at pH > 4.4; a.u., arbitrary units.



Fig. 4. UV-vis spectra for titania (Degussa)silica composite aerogel, titania (aerogel)-silica composite aerogel, titania aerogel, and silica aerogel.

the presence of insulating silica, a conduction threshold must be achieved for the carbon component so that an electronic path is created through the aerogel network.

We prepared carbon-silica composite aerogel monoliths (with base-catalyzed silica sol) that exhibit end-to-end conductivity at \geq 6.4 vol % of Vulcan carbon black (35). Nitrogen physisorption measurements (Table 1) indicate that this composite is highly porous, with a surface area weighted by the carbon component. Acid-catalyzed Vulcan carbon-silica aerogel composites are not conductive, even when the carbon fraction is increased to 30 vol %, which is consistent with the differences in the 3D silica structure derived from acid- or base-catalyzed hydrolysis and polycondensation. Base-catalyzed silica is composed of silica colloids with roughened surfaces arranged in a "pearl necklace" structure (7), whereas acid-catalyzed silica consists of highly ramified, polymeric silica chains (36). The former structure is much more porous than the latter, permitting connectivity of the Vulcan carbon between pores, whereas the branched nature of the latter leads to many "dead ends" and concomitant isolation of the carbon particles within the silica (37).

Another potential application for carbon-silica composite aerogels is as low temperature-processible black materials, for example, as opaque or low-reflectivity monoliths and coatings. Although light from an impinging He-Ne laser readily transmits through a pure silica aerogel, no light passes through a carbon-silica composite aerogel, as evidenced by the lack of a visible beam of light through a pure silica aerogel placed after the composite. Light scattering at the surface of the carbon-silica composite aerogel can be minimized by roughening the surface.

The use of silica sol as a nanoglue allows the design of nanoscale mesoporous platforms to the requisites of a desired application or property, because the composite maintains the surface and bulk attributes of each of its components. The specifics of the application will dictate the choice of sol-gel chemistry, the choice of guest, and the choice of molecular or biomolecular modifiers of the surfaces of the sol-gel host or the guest.

References and Notes

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mixing for 15 s, the dispersion was poured into small vials just before gelation. When adding solid at >50 vol %, the sol was added to a vial containing the solid, which was then sealed and shaken vigorously until gelation occurred, in order to ensure homogenous dispersion of the solid in the gel. Stirring or shaking is preferred over ultrasonication, because certain solids (carbons or polymers) will phase-separate during sonication. The gelation time is dependent on the type and amount of catalyst used and on the solid incorporated: typically, for a 15-ml total volume of silica sol, 0.7 ml of 30% NH₄OH (base-catalyzed gels; gelation time of 1.5 min) or 0.07 g of HCl (acid-catalyzed gels; gelation time of 3 min) was used. To date, the only solid we have found that affects the gelation time relative to neat silica sol is titania aerogel, for which the gelation time decreases proportionately to the amount of solid added. The composite gels are aged for no longer than 10 to 20 min before washing steps are initiated.

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- 29. The silica aerogel, titania aerogel, and titania (aerogel)—silica composite aerogel are transparent, so spectra were obtained for aerogel monoliths. Because the titania (Degussa)—silica composite aerogel scatters light in all UV-vis regions, a powder of the composite was mixed with pure silica aerogel and pressed into a pellet, and the absorption spectrum of the pellet was then measured.
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