

materials with electrical, magnetic, or optoelectronic properties through insertion of specific molecular or ionic species into the SGS hybrid solids.

Experimental

Synthesis: Lamellar organosilicic mesophases (SGS-L) were prepared by hydrolysis of *n*-octadecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride (2.39 g, ABCR Company) as a 60 % methanol solution in the presence of either NaOH or HCl (1.81 mL, 1 N). The product is immediately formed and was filtered, washed with water/methanol (1:1), and dried at 100 °C under vacuum.

Hexagonal organosilicic mesophases (SGS-H) were prepared by hydrolysis of TEOS (2.41 g) in a solution prepared from *n*-octadecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride (2.39 g) in NaOH (7.23 mL, 1 N). The resulting gel was stirred overnight at 25 °C. The product was recovered as described for SGS-L.

For the ion-exchange reactions, dried SGS samples (100 mg) were added to different aqueous salt solutions. The mixtures were stirred over 18 h. The final exchanged products were collected by filtration, washed, and dried at 100 °C.

Characterization: X-ray diffraction patterns were collected using a X'Pert Philips diffractometer equipped with a rotating anode and a CuK α radiation ($\lambda = 0.15418$ nm). High-resolution ^{29}Si MAS-NMR spectra of powdered samples were recorded at 79.94 MHz by spinning the samples at the magic angle in a Bruker MSL-400 spectrometer at RT equipped with a Fourier transformation unit. The spinning frequency was in the range of 4000–5000 Hz. Time intervals of 5 s between successive accumulations were selected for the Si nuclei in order to avoid saturation effects. 1600 accumulations were recorded. Tetramethylsilane was used as internal reference. Transmission electron microscopy (TEM) images were recorded on a JEOL 2000 FX microscope operating at an accelerating voltage of 200 kV.

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“Smart” Glasses: Molecular Programming of Rapid Dynamic Responses in Organosilica Sol–Gels**

By Mukti S. Rao and Bakul C. Dave*

Materials that can sense signals and produce a definite dynamic response in the form of a change in shape or size—the so-called “smart” or “intelligent” materials—are useful for many applications including design of shape-memory systems, drug delivery devices, chemical valves, artificial muscle mimics, and actuators.^[1–3] In this context, polymer hydrogels, which undergo swelling or shrinkage in response to an applied stimulus, have been the focus of intense research in recent times.^[4–6] However, the poor structural and mechanical integrity of conventional hydrogels, coupled with their typically long response times, remain critical issues that severely limit their practical usefulness. Consequently, the design of efficient response-active materials that are also mechanically rigid has been a desirable goal. Herein, we describe a strategy to elicit dynamic responses from a silica-based material prepared using the sol–gel process. Starting from a judiciously selected molecular precursor, the sol–gel reaction yields a solid-state glass—a mechanically robust yet elastic material—that is capable of generating dynamic responses when subjected to different physicochemical stimuli.

Movement is a distinctive feature of animate objects. Conversion of different forms of energy or signals into mechanical action is the key factor responsible for dynamic responses associated with movement and motion in living as well as artificial systems. Consequently, materials that can make this conversion and generate dynamic responses offer appealing technological prospects for the design of active elements (or

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actuators) for robotics and related intelligent systems.^[7] However, a rational design of active materials with predetermined responsiveness still remains an elusive goal. We report here a strategy to introduce dynamic responses in a porous silica-based glass by using a precisely modified sol-gel precursor. The approach may be generalized to prepare a variety of novel active materials and devices with molecularly programmed “smart” responses.

The sol-gel method for the synthesis of glasses begins with molecular precursors,^[8] and therefore it is possible to use chemical approaches to tailor the structure and properties of the parent silica sol-gel through the choice of the precursors.^[9] Our strategy for making a dynamically responsive sol-gel is based on a molecular design approach, which involves the use of the organically modified bis[3-(trimethoxysilyl)propyl]ethylenediamine (enTMOS) precursor, $(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$.^[10] The product sol-gel exhibits bulk volume changes to generate active mechanical responses with respect to several environmental variables.^[11] The effectiveness of these materials for generating dynamic responses is demonstrated by evaluation of a prototype tweezer-shaped device that can open and close when subjected to changes in temperature, pH, and electrical potential.

One of the vital criteria for generating a stimulus-induced dynamic response includes the occurrence of a bulk volume transition, which may be initiated by alteration of noncovalent interactions within a material and a subsequent expulsion or intake of water.^[1-6] The overall design strategy for selecting the enTMOS precursor was based on several factors that facilitate such dynamic responses to different environmental variables. First, the use of the alkoxodisilane precursor with a long-chain spacer unit forms a material with enlarged pores. Such enlarged pores increase retention of the aqueous phase in the porous network,^[10] and since the swelling and shrinkage mechanism of hydrogels is related to water intake and expulsion, respectively,^[1-6] a highly porous structure is more likely to exhibit a pronounced structural change. Second, the use of a precursor modified with an organic group yields elastic sol-gels. Because elasticity enhances the degrees of translational freedom at the molecular level, it was expected that the enTMOS-derived materials would undergo a volume change without catastrophic destruction of the sol-gel network when a stimulus is applied. Third, the proper combination of hydrophilic amino and hydrophobic alkyl groups enables control over the noncovalent interactions of the material with water. Finally, the ionizable amino groups in the precursor impart volume sensitivity with respect to changes in pH and ion concentration.

In order to obtain a precise quantitative measure of shape changes with respect to different stimuli, we used sol-gels with a tweezer-type architecture (Figs. 1a,b) formed by placing a polystyrene wedge in the liquid sol prior to its gelation, which was removed after the gels had aged. The distance between the arms of the tweezers was used to quantify the mechanical responses: Under the application of an external stimulus the distance between the arms of the tweezers varies, and this can be easily measured using an optical microscope.

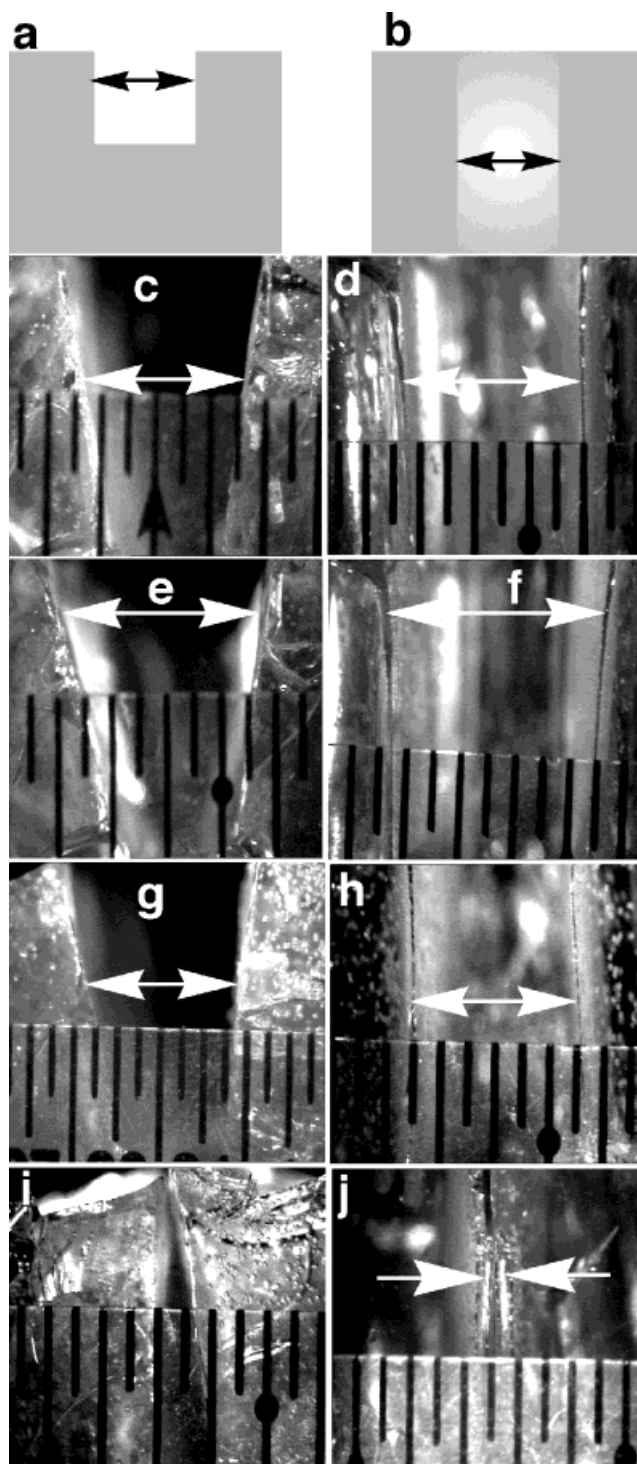
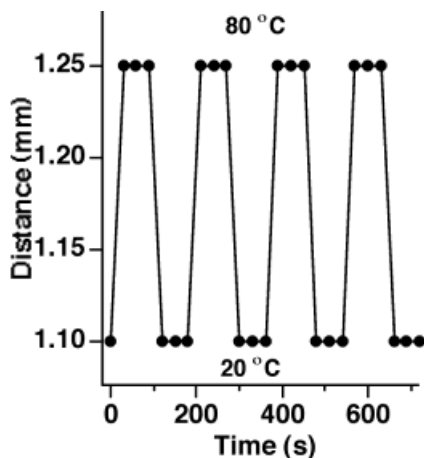


Fig. 1. The tweezer-type sol-gels are shown schematically as their a) side and b) top views, highlighting the distance between the arms of the tweezers. The images underneath capture the effects of temperature on the tweezers (each unit on the scale represents 0.5 mm). The tweezers are shown as their c) side and d) top views at 20 °C and as their e) side and f) top views after their immersion in a water bath at 80 °C for 5 min. On increasing the temperature the distance between the arms of the tweezers increased by about 0.5 mm. The images underneath were taken from tweezers prepared in 0.1 M acetate buffer when exposed to water. The tweezers are shown as their g) side and h) top views for the as-prepared tweezers and as their i) side and j) top views after their immersion in water for 4 h. As a result of exposure to water, the distance between the arms of the tweezers decreased such that the tweezers totally closed.

An increase in the hydrophobicity of a material at elevated temperatures is a characteristic of environmentally responsive polymers,^[3-6] and therefore the enTMOS-derived glasses were first evaluated for their shape-sensitivity to temperature variations. The tweezers were placed in a water bath and subjected to temperatures of 20 °C and 80 °C. The tweezers opened at high temperature and reversibly closed to the original state when the temperature was lowered (Figs. 1c-f). The response time for these dynamic changes is very short. At the higher temperatures, increased hydrophobic interactions between the organic groups led to expulsion of water from the porous structure, and the material shrunk. As a result, the distance between the arms increased and the tweezers opened. Lowering the temperature induced an intake of water and reswelling of the gel, which caused the distance between the arms to decrease and the tweezers closed.

Due to the presence of ionizable amino groups in the material, it was expected that the sol-gel would show a sensitivity to pH. We measured the dynamic response of the gels prepared in an acidic medium. For this purpose, we made the gels by mixing the enTMOS precursor and 0.1 M (pH 4.5) acetate buffer (each 1 mL). When these gels were exposed to water, the distance between the arms of the tweezers reduced, from an initial distance of 3 mm (Figs. 1g,h) to total closure when placed in water (Figs. 1i,j). The closure is caused by swelling of the material. At low pH, the amino groups are protonated and minimization of electrostatic repulsion between the chains is achieved by a rapid intake of water and concomitant swelling.

The temporal responses of the tweezers' operation with respect to temperature and pH variations are shown in Figures 2 and 3. The actual movement of the arms of the tweezers was quite rapid. Figure 2 shows the changes in distance between the arms of the tweezers with temperature. Data points were collected at 30 s intervals. The distance changed quite rapidly and the movement of the tweezers was completed within 30 s. A consecutive opening-closing movement of the tweezers was observed. It is particularly important to note that the overall movement was very well defined and the changes were reproducible, distinct, and occurred in discrete steps.



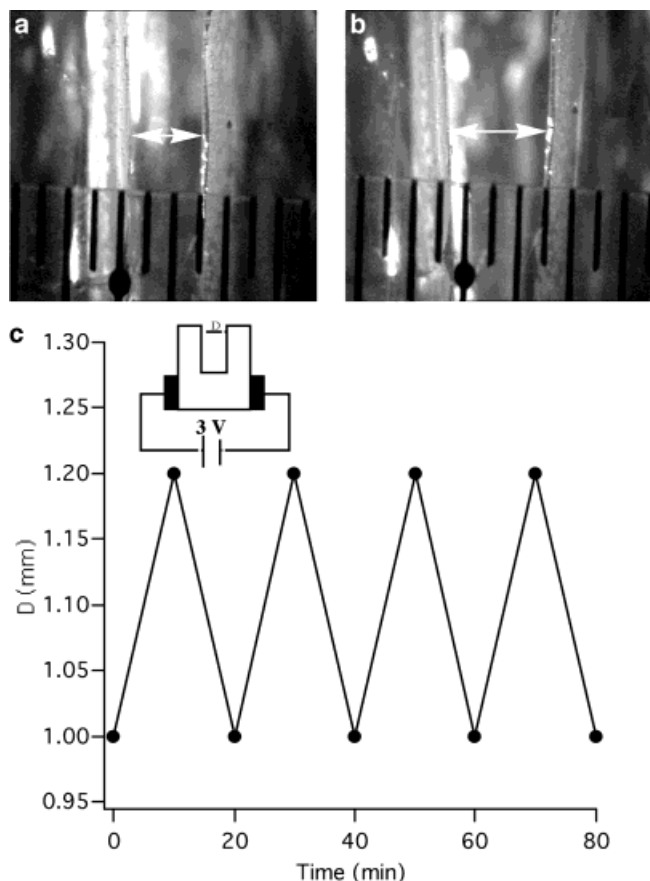


Fig. 4. Electrochemomechanical response of the tweezers. The images show the top view of the tweezers a) before and b) after application of a 3 V potential. c) The reversible changes in the distance D between the arms of the tweezers under a modulated applied potential of 3 V with time. The tweezers opened when the potential was applied to the base of the tweezers; upon switching the potential off, the tweezers closed to the original value. Inset: the schematic of the experimental setup used to measure the response of the tweezers. The potential was applied using press-on aluminum foil electrodes.

hydrophobic functional groups do not undergo dynamic changes in response to environmental variables, and the presence of *both* hydrophobic and hydrophilic residues in a precursor is vital to generate bulk dynamic responses.

From the above observation, the environmentally sensitive behavior of the enTMOS gels can be ascribed to the presence of hydrophilic amino and hydrophobic methylene groups in the network. Figure 5 shows the molecular units present in the enTMOS sol–gel according to their affinity for water; the hydrophilic groups are represented by light shading whereas the hydrophobic organic groups are represented by dark shading. In the swollen state, the pores hold a substantial amount of water stabilized by hydrogen bonding interactions with the hydrophilic siloxane and amino groups. In the shrunken state, the hydrophobic interactions between the organic functionalities predominate and water is expelled from the porous structure. The transition between the swollen and the shrunken state is stimulated by an externally applied physicochemical variable (Fig. 5). The environmental sensitivity and dynamic responses of the enTMOS sol–gels mainly arise from specific movement of molecular domains due to variations in non-

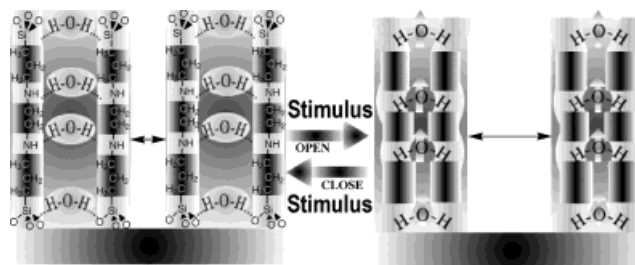


Fig. 5. Schematic depiction of molecular mechanism of dynamic responses associated with operation of the enTMOS-derived tweezers. The opening (shrinkage) and closing (swelling) of the tweezers is mediated by an applied stimulus, through which the non-covalent interactions of the gel with water are altered and result in a loss or gain of water. A sequential change in distance between the arms enables the operation of reversible tweezing action.

covalent interactions in the spacer group. Consequently, the observed volume changes are smaller as compared to organic polyelectrolytic hydrogels. However, such a localized response suggests that the enTMOS sol–gel system possibly undergoes only minimal entropic losses due to short-range movements of the sol–gel network during the conversion of energy to mechanical action. This is consistent with the rapid responses observed for the enTMOS system, which indicate a more efficient conversion of energy to useful work.

Inasmuch as the dynamic stimulus–response behavior was molecularly programmed into the enTMOS materials by a selective choice of the precursor, the observed results are consistent with the molecular design approach. The molecular mechanisms responsible for generating active responses in enTMOS sol–gels are similar to those for polymeric hydrogel systems.^[4–6] Temperature, pH, and ions induce changes in its water affinity, and the consequent loss or uptake of water are known to be responsible for shrinkage or swelling in polymeric hydrogel systems, and similar mechanisms operate in the enTMOS system. Additionally, electrokinetic diffusion of mobile ions under an applied electric field is associated with induced mechanical deformations in polyelectrolyte gels,^[4–6] and the electrochemomechanical behavior of the enTMOS sol–gels is analogous. The strategy described here offers a potentially powerful approach for designing a diverse range of stimulus-responsive sol–gel materials, whose properties may be tailored precisely through systematic control over both the composition of product materials and the extent of environmental sensitivity, and ultimately to materials with tunable active responses.

In conclusion, we have demonstrated the feasibility of imparting environmental sensitivity to sol–gel-derived silica-based glasses. The dynamic stimulus–response behavior in these glasses results from a deliberate incorporation of a response-active bis(propyl)ethylenediamine structural unit. The approach illustrates molecular programming of environmental sensitivity into silica-based materials via appropriate functional modification of precursors. An important aspect of these materials is that they combine all the essential functions of an intelligent material in a single-component monolithic unit; they are able to sense the external stimulus, translate the stimulus into mechanical action, and generate an active dy-

namic response. Since the sensing–actuating mechanism is an intrinsic property of the enTMOS sol–gel, the resulting monolithic device elements are simple, self-sufficient, and self-sustaining under a given applied stimulus. Conversion of different forms of physicochemical potential to mechanical activity underlies the basis of actuation, and the mechanically rigid sol–gel-derived materials and devices provide an example of a technologically compatible intelligent system for practical applications as artificial muscle mimics and as micromechanical devices.

Experimental

The sol–gels were prepared by hydrolysis of the enTMOS precursor (Gelest Inc., Tullytown, PA) followed by gelation in a polystyrene cuvette. A typical preparation involves mixing an equal volume of water and the precursor. Upon addition of water, hydrolysis and condensation of the siloxane units give rise to a solid porous sol–gel. The freshly formed sol–gels were allowed to age for one day to allow the gelation to go to completion. These aged materials were used for all the experimental data reported in this paper.

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Reversal of Circular Bragg Phenomenon in Ferrocholesteric Materials with Negative Real Permittivities and Permeabilities

By Akhlesh Lakhtakia*

Dielectric and magnetic materials are ubiquitous. Their linear electromagnetic response properties are characterized by permittivity and permeability dyadics that depend on the frequency of excitation and comprise complex-valued scalar components. The permittivity and the permeability dyadics (i.e., second-order tensors) of an isotropic material reduce to complex-valued scalars. The real parts of these scalars can be negative or positive, but the latter possibility is the normative one of the two, as almost any undergraduate electromagnetics textbook will show. However, the former possibility does exist for natural materials such as metals, plasmas, and ferrites.^[1,2] Most recently, composite materials that effectively have both a negative real permittivity and a negative real permeability in a certain frequency range have been fabricated and satisfactorily tested,^[3,4] notwithstanding the discounting of anisotropy, inhomogeneity, and dissipation in the sample materials.^[5]

Technological bonanzas have been proffered, provided homogeneous, isotropic, and virtually non-dissipative materials with negative permittivity and negative permeability can be economically manufactured.^[5–7] These potential benefits are based on the opposite directions of the phase velocity and the velocity of energy transport in these materials. Available results indicate that these materials would be realized in the form of multilaminar slabs, each lamina itself being anisotropic due to the imprinting of various features thereon.^[4,7] Feature geometries other than the only one in current use will also arise, sooner or later. These open up the possibility of an entirely new class of prospective materials: ferrocholesterics with negative permittivity and negative permeability. This communication is devoted to these unidirectionally inhomogeneous materials.

About twenty years before the discovery of cholesteric liquid crystals by Reinitzer in 1888,^[8] Reusch^[9] presented structurally similar materials made from uniaxial dielectric laminas, which can possibly be fabricated as unidirectional fibrous composites. The laminas are identical, with the sole optic axis lying in the laminar plane. The laminas are stacked sequentially, the optic axis in any particular lamina offset by a small angle in the laminar plane from the optic axis of the lamina lying immediately below it. The successive optic axes rotate helicoidally, and the optical response properties of the entire structure resemble those of a cholesteric liquid crystal at frequencies below a certain maximum.^[10] The optical response

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