



Photoresponsive Nanocomposite Formed by Self-Assembly of an Azobenzene-Modified Silane**

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Mesoporous materials made by surfactant-directed self-assembly (SDSA) have been of great interest in the past decade because of their potential applications in catalysis, membrane separations, adsorption, and chemical sensing.^[1–6] In SDSA, inorganic moieties formed by alkoxide hydrolysis interfacially coorganize with hydrophilic surfactant head-groups to form periodically ordered hybrid mesophases. After condensation and removal of surfactant molecules by heat or solvent extraction, a periodic mesoporous inorganic matrix is created. To expand the range of applications as well as create new properties, various organic functional groups have been covalently incorporated onto the pore surfaces of mesoporous materials, including phenyl, octyl, aminoalkyl, cyanoalkyl, thioalkyl, epoxy, and vinyl groups.^[6–10] However, to date, these modifications have provided mainly “passive” functionality, such as controlled wetting properties, reduced dielectric constants, or enhanced adsorption of metal ions. By comparison, materials with “active” functionality would enable properties to be dynamically controlled by external stimuli, such as pH, temperature, or light. In an effort to make such active hybrid materials, Ogawa et al. intercalated azobenzene moieties within a clay (magadiite), which resulted in a hybrid layered composite in which restricted photoisomerization caused the *d* spacing to change reversibly by 0.6 Å upon exposure to UV and visible light.^[11] Several groups have reported^[12,13] or suggested the formation of photoactive hybrids through SDSA of azobenzene or pyridylethylene bridged silsesquioxanes. For a lamellar mesostructure, Brinker and co-workers showed the *d* spacing to be optically controllable through photoisomerization of the azobenzene moiety before or after self-assembly. Alvaro et al.^[13] doped

1,2-bis(4-pyridyl)ethylene in the wall of a hexagonal mesoporous silica and provided preliminary evidence of photo-induced changes in the surface area and pore volume.

As shown in Figure 1, the incorporation of covalently bonded “switchable” ligands as pendant groups (as opposed to bridging groups^[12–14]) within a porous (rather than a layered^[11,12]) framework is expected to result in nanocompo-

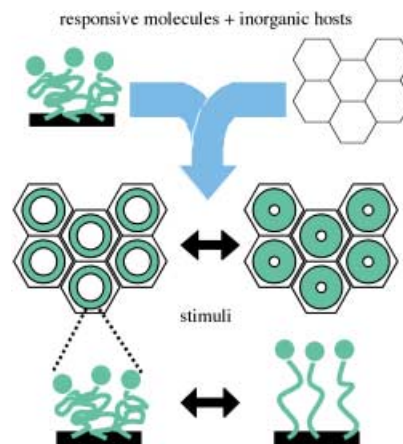


Figure 1. Concept of responsive nanocomposites: Organization of stimuli responsive ligands within a 3D porous framework imparts new molecular-level functionality, which is useful for opening and closing a nanoscale valve. (Adapted from Bruce Bunker, unpublished work).

sites, in which the pore size, surface area, and adsorptive properties are externally controllable. In such synergistic nanocomposites, the 3D organization of the responsive ligands allows the transduction of photo, chemical, or thermal energy into a useful mechanical response of interest for molecular valves or gates, with potential applications in smart gas masks, membranes, controlled release systems, and new types of externally controlled micro/nanofluidic-channel systems. In addition, the rigid framework could serve to enhance the mechanical, chemical, and thermal stability of the responsive moieties, thus fostering their integration into devices.

Herein we report the SDSA of a novel photoresponsive azobenzene-containing organosilane, 4-(3-triethoxysilylpropylureido)azobenzene (TSUA) into an ordered, periodic silica framework to make photoresponsive nanocomposites. Azobenzene derivatives were selected because of their well-studied response to light.^[15–18] UV irradiation of the *trans* isomer causes transformation to the *cis* isomer. Removal of the UV radiation, heating, or irradiation with a longer wavelength switches the system back to the *trans* form.

Photoresponsive thin-film nanocomposites were fabricated by an evaporation-induced self-assembly (EISA) procedure by using the nonionic surfactant, Brij56 ($C_{16}H_{33}(OCH_2CH_2)_nOH$, $n \sim 10$), as a structure-directing agent.^[19] TSUA was mixed with tetraethyl orthosilicate (TEOS) in a homogeneous ethanol/water solution with an initial surfactant concentration less than the critical micelle concentration (cmc) and an acid concentration designed to minimize the siloxane condensation rate, thereby avoiding

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premature gelation, which would frustrate the self-assembly process. In EISA, ethanol evaporation accompanying spin or dip coating enriches the depositing film in water, surfactant, and silica constituents, which results in the self-assembly of silica-surfactant micelles and their further organization into liquid-crystalline mesophases.^[2,19] For TSUA-containing sols, we suspect that the amphiphilic nature of the hydrolyzed TSUA molecule will position the hydrophobic propylureidoazobenzene groups in the hydrophobic micellar cores and that the silicic acid groups will be coorganized with hydrolyzed TEOS moieties at the hydrophilic micellar exteriors. In this fashion, TSUA is ultimately incorporated onto the pore surfaces with the azobenzene ligands disposed towards the pore interiors. A subsequent solvent extraction^[7,8] results in a mesoporous silica framework derivatized with azobenzene ligands, which are isomerizable by light and thermal stimuli (Figure 2). The dimensional change of the propylureidoazobenzene ligand associated with this isomerization mechanism is estimated to be 3.4 Å based on molecular modeling with Chem3D Pro 5.5 software (Figure 2).

Figure 3 shows a representative X-ray diffraction (XRD) pattern and cross-sectional transmission electron microscopy (TEM) image of a prepared nanocomposite film. The XRD pattern shows a strong reflection at 2.8 nm and a weaker reflection at 1.4 nm. The TEM cross-sectional image and electron diffraction pattern (Figure 3, inset) are consistent with a cubic mesostructure with an average center-to-center pore spacing of 5.6 nm (measured directly from the TEM image and calculated from the electron diffraction pattern) in the direction perpendicular to the substrate. A TEM plan-view image shows a similar pattern. Based on these results, we suggest that the (100) plane of the body-centered cubic (BCC, $Im\bar{3}m$ space group) mesophase is oriented parallel to the substrate, consistent with previous reports,^[20,21] which allows the two XRD peaks to be assigned to the d_{200} and d_{400} reflections, respectively. The BCC mesophase is distorted slightly because of greater shrinkage in the direction perpendicular to the substrate than parallel to the substrate resulting from siloxane condensation.

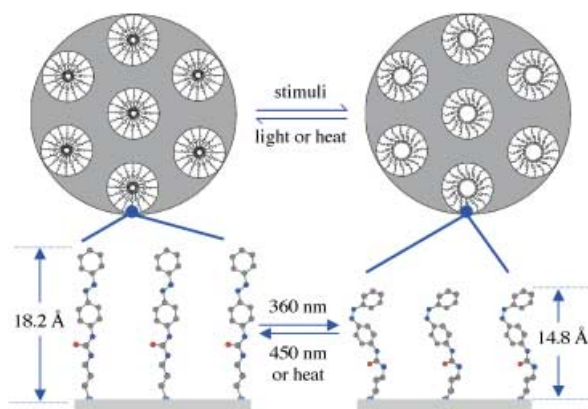


Figure 2. Photoresponsive nanocomposites prepared by EISA. The *trans* or *cis* conformation of azobenzene unit was calculated using Chem3D Pro 5.5 molecular modeling analysis software. Atom labels: C: grey, O: red, N: dark blue, Si: blue, H atoms are omitted.

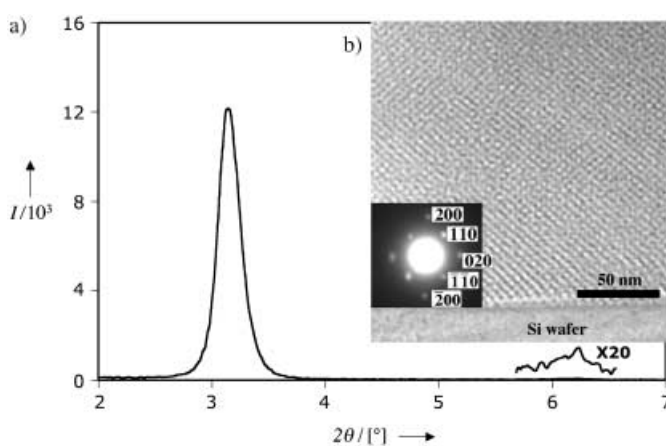


Figure 3. a) XRD and b) TEM cross-section image of a photoresponsive nanocomposite. The inset is an electron diffraction pattern corresponding to the [001] zone axis.

UV/Vis spectroscopy was used to characterize the photo and thermal responsiveness of the incorporated azobenzene ligands. Figure 4 shows the UV/Vis spectra of thin films after exposure to varying conditions of UV irradiation (8 W, $\lambda = 302$ nm), room light, or heat. The absorption band at 350 nm is attributed to the $\pi \rightarrow \pi^*$ transition of the *trans* isomer and the band at 460 nm to the $n \rightarrow \pi^*$ transition of the *cis* isomer. UV irradiation causes a progressive *trans* to *cis* isomerization as noted by the decrease of the 350 nm band and increase of the 460 nm band, with a photostationary state reached after 30 minutes (Figure 4 spectrum b). Exposure to room light or heat caused the reverse isomerization (*cis* \rightarrow *trans*). For example, from the photostationary state (Figure 4 spectrum b), a room-light exposure resulted in a progressive increase in the intensity of the 350 nm absorption band and a progressive decrease in the 460 nm absorption band (Figure 4 spectra c–f). A lengthy (12 hour) room-light exposure resulted in an increase in the intensity of the 350 nm absorption band close to that of the prepared film. Alternatively heat treatment (100 °C, for 5 minutes in the dark) caused the intensity of the 350 nm absorption band to exceed

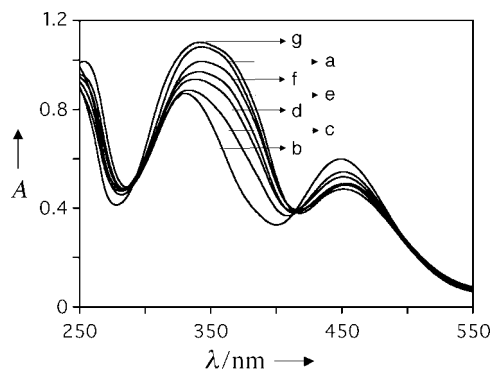


Figure 4. Photo and thermal isomerization of azobenzene ligands in the nanocomposite films prepared with Brij56 template. a) Prepared; b) after UV irradiation for 30 minutes; c, d, e, f) after room-light exposure of the sample (b) for 3, 15, 35, and 60 minutes, respectively; g) after heating the sample (b) to 100 °C for 5 minutes.

that of the prepared nanocomposite film (Figure 4 spectrum g), which indicates that a certain amount of azobenzene ligands were in the *cis* conformation in the prepared films. These results, which are completely reversible, demonstrate the facile photoisomerization characteristics of the pendant azobenzene ligands in the ordered porous nanocomposite. As a control experiment, we prepared films with the same sol in the absence of Brij56. In this case, the azobenzene ligands were randomly incorporated into a microporous silica matrix and exhibited no detectable photoisomerization. Similarly we observed no photoisomerization for the ordered self-assembled films prior to solvent extraction of the surfactant templates. Only upon surfactant removal did we create the pore volume required (estimated as 127 \AA^3)^[22] for photoisomerization. These results unambiguously locate the photosensitive azobenzene ligands along with surfactant within the uniform nanopores of the self-assembled films, and emphasize the need to accommodate the steric demands of the photoisomerization process by engineering the pore size (as noted previously for adsorbed azobenzene dyes^[18]) and by positioning the photoactive species on the pore surface. Correspondingly, nanocomposite films prepared by using a triblock copolymer surfactant $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (P123), which had larger pores (about 6.5 nm in diameter), exhibited a faster and more complete *trans* to *cis* isomerization, close to that of TSUA in EtOH, presumably because the azobenzene ligands were less sterically constrained (see Supporting Information).

Studies of the photoresponsive mesoporous films by ^{29}Si MAS NMR spectroscopy (MAS = magic-angle spinning) showed T^2 , T^3 , Q^2 , Q^3 , and Q^4 resonances at $\delta = -52.81$, -62.11 , -93.18 , -99.69 , and -107.12 ppm, respectively. The total amount of T ($T^2 + T^3$) is 11 %, consistent with the molar ratio of TSUA/TEOS added in the starting sol. The extents of condensation of the T and Q species are 93 % and 82 %, respectively, thus proving covalent attachment of the azobenzene ligands to the pore surface and demonstrating the stability of the Si–C bonds throughout the self-assembly and extraction processes.

Thermogravimetric analysis (TGA) of photoresponsive mesoporous materials in air showed about 16 % weight loss from 194 to 288 °C and about 18 % weight loss from 288 to 620 °C, the latter arising from the decomposition of the azobenzene ligands. Analysis of the N_2 sorption isotherms^[23] by SAW techniques (SAW = surface acoustic wave) after calcination at 450 °C, to remove the azobenzene ligands, indicated a pore diameter of 2.5 nm and surface area of $619 \text{ m}^2 \text{ g}^{-1}$. Taking into account film shrinkage during calcination ($\sim 30 \text{ vol} \%$) versus solvent extraction ($\sim 10 \text{ vol} \%$), we estimate pore diameters to be about 3.6 nm and 3.2 nm before and after surfactant removal, respectively, thus requiring the *trans* isomers to be at least slightly tilted from the surface normal in of the extracted films. Based on surface area and weight loss, the surface coverage is estimated to be about 1.2 azobenzene ligands nm^{-2} , which corresponds to an average ligand-to-ligand spacing of $(1/1.2 \text{ nm}^2)^{1/2} = 0.9 \text{ nm}$. By using a molar absorption coefficient of $2.59 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for the *trans* isomer (determined from UV/Vis spectra of TSUA solutions in ethanol), we calculated the *trans* isomer concentration in the films to be 1.55, 1.52, and 1.12 M, respectively, for

samples g, a, and b in Figure 4. Both the surface coverage and the molar concentrations of azobenzene ligands in the self-assembled films greatly exceed those attainable by dye adsorption in mesoporous films.^[18]

As illustrated in Figure 2, the positioning of photoisomerizable ligands on the surface of uniformly sized pores should enable photo control of the pore size.^[*] Ideally, with radially oriented azobenzene ligands, we can expect to change the pore size by about 6.8 Å. This optomechanical actuation could serve to open or close a nanopore or change the transport-limiting pore size in a membrane. Additionally, there is a significant dipole moment change associated with *trans*–*cis* isomerization (0–3 D),^[24] which could strongly influence ion transport. Optical control of both pore size and dipole moment in a uniform silica nanopore could lead to robust, synthetic ion channels needed for practical stochastic sensing devices.^[25] In this regard it is noteworthy that the modification of a gramicidin A channel with a single azobenzene moiety enabled optical switching of ion fluxes.^[24]

Experimental Section

TSUA was prepared by an isocyanato–amino coupling reaction between triethoxysilylpropyl isocyanate and 4-phenylazoaniline, then purified by recrystallization. In a typical synthesis of a photoresponsive nanocomposite thin film, Brij56 (0.27 g) and TSUA (0.26 g, 0.58 mmoles) were dissolved in EtOH (6 mL) which contained TEOS (1.0 g, 4.8 mmol; Aldrich, 99.99 %). After addition of HCl (0.5 mL, 0.1 M), the solution was sonicated for 3 minutes. The final molar ratio of TSUA, TEOS, EtOH, Brij56, H_2O , and HCl was 1.0:8.2:177:0.68:47.5:0.085. The mixed sol was aged for 30 minutes at room temperature and then deposited on silicon substrates by dip coating, spin coating, or casting. The surfactant molecules in the mesostructured film were extracted by refluxing the condensed thin films in an acidic ethanol solution according to previously reported procedures.^[7,8]

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[*] As noted by one reviewer it would be of interest to measure the accessible nanocomposite pore volume for the *trans* and *cis* forms of the azobenzene. We have attempted this using SAW-based nitrogen sorption. However, to get meaningful data we need to degas the coated SAW device for several hours. By using UV/Vis spectroscopy we have determined that in the dark the *cis* isomer converts into the *trans* form over a period of several hours. Thus, we are unable to acquire and legitimately compare nitrogen sorption isotherms of the *trans* and *cis* forms. However, in a preliminary experiment we modified the electrode of a photochemical cell with our photoresponsive film and, by using ferrocene as a molecular probe, performed a chronoamperometry experiment with and without UV exposure. We observed a reversible optically mediated response, which indicates the reversible photoregulation of mass transport.

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