Research Article

Photoresponsive Release from Azobenzene-Modified Single Cubic Crystal NaCl/Silica Particles

Xingmao Jiang,[1] Nanguo Liu,[2] Roger A. Assink,[3] Yingbing Jiang,[4] and C. Jeffrey Brinker[1, 3]

[1] *Department of Chemical and Nuclear Engineering and Center for Micro-Engineered Materials,*
   The University of New Mexico, Albuquerque, NM 87106, USA
[2] *SCB Innovation Accelerator, Dow Corning Corporation, 2200 W. Salzburg Road, P.O. Box 0994, Midland, MI 48686, USA*
[3] *Advanced Material Laboratory, Sandia National Laboratories, Albuquerque, NM 87185, USA*
[4] *Transmission Electron Microscopy Labs, The University of New Mexico, Albuquerque, NM 87131, USA*

Correspondence should be addressed to C. Jeffrey Brinker, cjbrink@sandia.gov

Azobenzene ligands were uniformly anchored to the pore surfaces of nanoporous silica particles with single crystal NaCl using 4-(3-triethoxysilylpropylureido)azobenzene (TSUA). The functionalization delayed the release of NaCl significantly. The modified particles demonstrated a photocontrolled release by trans/cis isomerization of azobenzene moieties. The addition of amphiphilic solvents, propylene glycol (PG), propylene glycol propyl ether (PGPE), and dipropylene glycol propyl ether (DPGPE) delayed the release in water, although the wetting behavior was improved and the delay is the most for the block molecules with the longest carbon chain. The speedup by UV irradiation suggests a strong dependence of diffusion on the switchable pore size. TGA, XRD, FTIR, and NMR techniques were used to characterize the structures.

1. Introduction

Mesoporous silica with well-defined structures has attracted much attention for controlled release of dyes [1], drugs [2, 3], perfumes, and flavorings [4, 5]. Recently nanoporous spherical silica particles with ordered structures have been prepared by aerosol-assisted self-assembly [6]. Ordered mesoporous core-shell silica particles with single crystal NaCl nanocube or Ce core have also been synthesized [7, 8], and the core-shell structure [8] has been shown effective for corrosion inhibition of aluminum alloy AA2024-T3. The functionalization of pore surfaces by organic groups regulates the hydrophobicity and therefore the release behavior, and the hydrothermal stability of the silica particles has also been improved. Long-term (years) protection of metals and alloys requires the release of the encapsulated corrosion inhibitors to the target surface in a well-controlled manner. Tailorable inherent structure properties such as particle size, pore size, pore connectivity, structure stability, and surface chemistry, are key factors for release behavior. Active transport triggered by external stimuli such as light [4], pH [9], temperature [10], and electric field [11] are required for a lot potential applications such as drug release, optical devices, and sensors. It also provides additional flexibility for release control. Azobenzene ligands are well known for their active response to light and heat. For example, the dipole moment of the azobenzene group can be reversibly switched between approximately 3D and 0D by cis-trans photoisomerization, resulting in an optical control of ion channel gating for Cs^+ and Na^+ movement through the pores [12]. The photoswitchable gates based on the extended trans and the shorter cis configurations of photoisomerizable azobenzene groups in the pore blockers regulated K^+ flow [13] in engineered K^+ channel, resulting in a remote control of neuronal firing. Azobenzene moieties bonded to cross-linked membrane reversibly changed the transport number of sulfate ions relative to chloride ions in electrodialysis [14]. The adsorbed azobenzene in zeolite-azobenzene membranes of ZSM-5 (MFI) and Faujasite-type (FAU) zeolites changed gas permeation by photoinduced switching [15]. Azobenzene-functionalized glassy polymer films demonstrated a photoresponsive gas permeability [16]. Liu et al.

succeeded in making a photoresponsive nanocomposite thin film by (evaporation-induced) surfactant-directed self-assembly (EISA) of an azobenzene-modified silane, 4-(3- triethoxysilylpropylureido)azobenzene (TSUA), and tetraethyl orthosilicate (TEOS) [17]. They went further to investigate the photoregulation of mass transport through a photoresponsive azobenzene-modified nanoporous membrane [18]. The optically switchable conformation of azobenzene ligands controlled the effective pore size and, correspondingly, transport behavior on the nanoscale.

In this paper we modified the pore surfaces of mesoporous silica particles of single crystal NaCl cube with TSUA. The extent of condensation increased from 92.4% to 96.45% after the modification. The functionalization delayed the release of NaCl significantly. The modified particles demonstrated a photocontrolled release. The photoresponsive release suggests a strong dependence of diffusion on the switchable pore size. The added amphiphilic solvents, propylene glycol, propylene glycol propyl ether, and dipropylene glycol propyl ether delayed the release in water, although the wetting behavior was improved, and the delay is the most for the block molecules with the longest carbon chain. A few techniques such as TGA, XRD, FTIR, NMR, and TEM were used to characterize the structures.

2. Experiment

2.1. Materials. TSUA was prepared in the method described elsewhere [19]. All chemicals were used as received. Tetraethyl orthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB), toluene, propylene glycol, propylene glycol propyl ether (98.5%), and dipropylene glycol propyl ether (98.5%) were obtained from Aldrich; NaCl was manufactured by J. T. Baker. Hydrochloric acid was VWR brand, while absolute ethanol was obtained from Aaper. Millipore deionized water was used for all experiments.

2.2. Particles Synthesis. Ordered mesoporous silica particles of single crystal NaCl cube were generated from TEOS as described in a previous work [9]. 1.07 g TSUA was added into 200 ml toluene dried beforehand by molecular sieve 4 A under stirring at 35°C. After the dissolution of TSUA in the solution, 2.5 g of the NaCl/silica particles were added into the solution refluxed at 90°C for 12 hr. The particles were centrifuged and washed six times using large quantity of hexane, and vacuum dried at 70°C for 2 days.

2.3. Characterizations. The mesostructures of the particles were verified using a combination of powder X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis/differential thermal analysis (TGA/DTA). The experiment procedures are the same as described elsewhere [7, 8]. For TEM nitrogen mapping, the particles were first dispersed in a toluene solution of poly(methyl methacrylate), dried, and then microtomed into 50 nm thin films.

NMR characterization of the particles was performed on a Bruker DRX 400 MHz instrument. The release behaviors
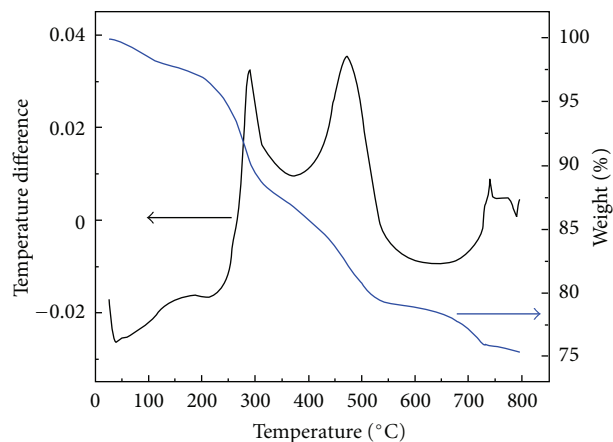

Figure 1: TGA/DTA plot of azobenzene-modified sample under air.

of the particles was checked by monitoring the conductivity of the solutions using VWR Corning 316 conductivity meter. Corning Acquire software was used to automatically record the data. A 100 ml quartz beaker from Ace Glass was used for UV ($\lambda = 360$ nm) irradiation, and a 200 W Hg-Xe arc lamp (ORIEL, model 66002) with optical filters was used as the light source.

3. Results and Discussion

As shown in Figure 1, the TGA/DTA of photoresponsive mesoporous materials in air showed about 10.5% weight loss from 177 to 357°C for dehydration of silanols in the silica structures and about 9.5% weight loss from 383 to 666°C and the decomposition of the azobenzene ligands. Considering the original NaCl/silica particles of a surface area of 796 m^2/g and pore size of 2.05 nm, the surface coverage is estimated to be about 0.67 azobenzene ligand nm^{-2}, smaller than the value, 1.2 azobenzene ligands nm^{-2}, reported for the photoresponsive nanocomposite formed by direct self-assembly of an azobenzene-modified silane [17].

The average axial distance in the pores between two adjacent azobenzene ligands is 2.3 A. The modification of pore surface is effective to anchor chemically the azobenzene ligands to pore surfaces.

The FTIR spectra were shown in Figure 2. The sample demonstrated strong absorption near 1047 cm^{-1} due to the –Si–O–Si– structure and broad absorption near 790 and 3478 cm^{-1} arising from Si–OH structure in the samples. There are three characteristic vibrational bands of the –NH–CO–NH– group: = 3344 cm^{-1} (N–H stretch), 1654 cm^{-1}, and 1543 cm^{-1} (C=O, stretching of amides). Besides, the sample showed characteristic absorption near 1200 cm^{-1} for aromatic amine and vibrational bands: 3030, 2945, 2928 cm^{-1} for aromatic C–H stretch. TEM image for azobenzene-modified particles in Figure 3 showed the ordered porous silica structures with single crystal NaCl. The count mean diameter for the particles is ~200 nm, and the geometric standard deviation is ~2. The single crystal NaCl has a size nearly half of the particle size. The silica shell thickness is around one-fourth of the particle size. The
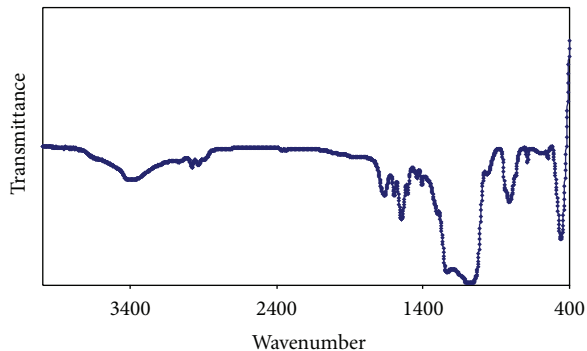
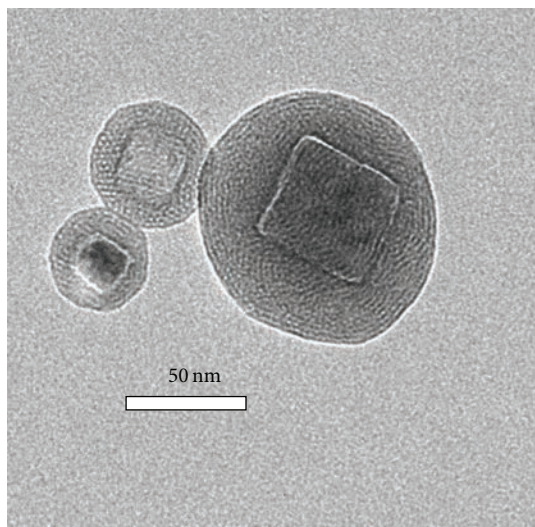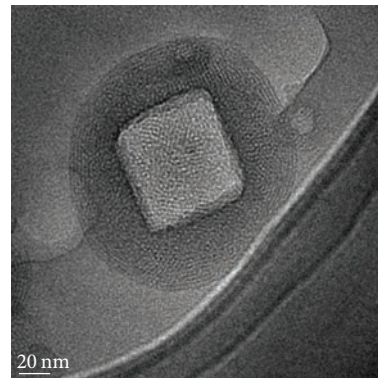Figure 2: FTIR spectrum for azobenzene-modified sample.

Figure 3: TEM image for azobenzene-modified sample.

(a)

(b)

Figure 4: Energy-filtered N mapping for cross-sectioned azobenzene-modified particle. (a) TEM image, (b) N mapping.

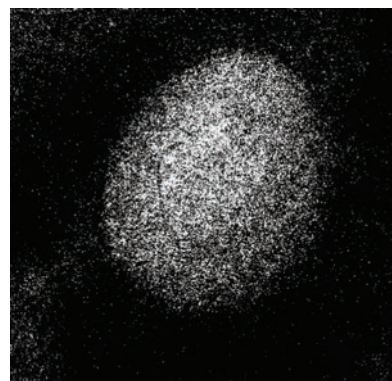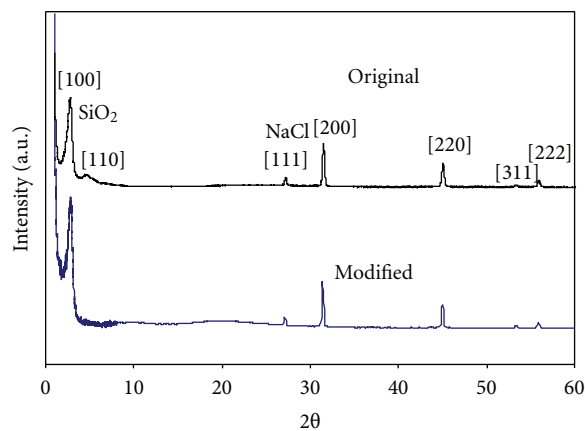Figure 5: XRD patterns for NaCl-silica core-shell structured particle samples.

TEM image obtained from ultramicrotomed sections for modified particle samples was shown in Figure 4. Based on the N mapping for the 50 nm ultrathin layer of microtomed sample, TSUA molecules penetrated well inside the particles, and the azobenzene ligands were covalently anchored within the particles uniformly.

The XRD patterns for the samples as shown in Figure 5 indicated that after the modification the particles keep both the orders for porous silica and crystal NaCl as also demonstrated in Figure 3.

As shown in Figure 6 and Tables 1 and 2, studies of the modified particles by ^{29}Si MAS NMR spectroscopy showed T1, T2, T3, Q2, Q3, and Q4 resonances at $\delta = -51, -57.6, -65.1, -90.6, -99.7$, and -108.4 ppm, respectively. 10.33% of the Si were T's, and 89.67% were Q's (the ratio of Si in T's to Q's is ~1 : 12 based on TGA/DTA data). The extent of condensation of the T species was 54.2%, and the extent of condensation of Q species increased from initial 92.4% to 96.45%, while only 0.49% of Q2 existed for modified particles. The treatment is effective to convert the –OH groups on pore surfaces and provided covalent attachment of the azobenzene ligands to the pore surface. The modified particles showed a delayed and

photoresponsive release at 25°C under a stirring at 300 rpm. Before the modification, the release is very quick; within 1 minute, all the NaCl molecules diffused into the solution (Figure 7). The external transport resistance is not negligible for the situation. As shown in Figure 7, the addition of long molecule solvent such as DPGPE delayed the release to some degree. However, after the modification, the particles showed a far different behavior. As shown in Figure 8, the releases
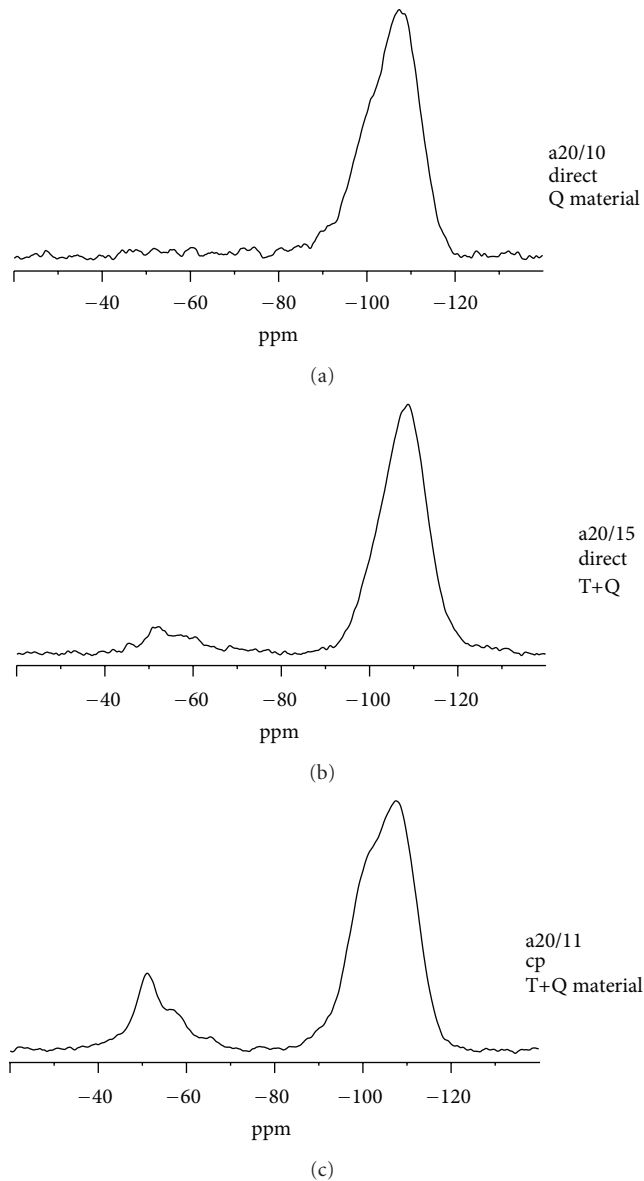
(a)

(b)

(c)

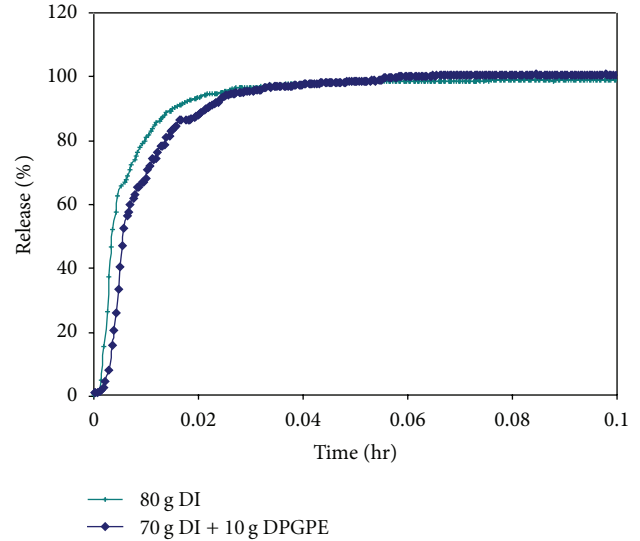FIGURE 6: ^{29}Si NMR spectra of NaCl/SiO$_2$ samples before/after modification.

FIGURE 7: Release profiles for NaCl/silica particles in DI water and water solution of DPGPE.

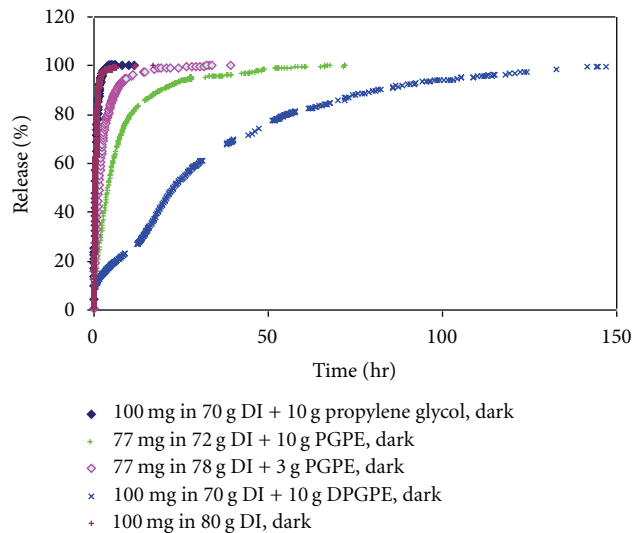
FIGURE 8: Release profiles for azobenzene-modified NaCl/silica particles in various solutions.

TABLE 1: NMR results for unmodified particle sample.

Si species	Shift (ppm)	Linewidth (Hz)	Integral (%)
Q2	−90.6	506	4.14
Q3	−98.9	620	22.15
Q4	−107.7	812	73.71

were delayed greatly. The concentrations got stabilized after ~4–150 hr release for modified particles in DI water added with various solvents. The delay depended on the amount and the molecular size of the added solvent. As common used amphiphilic solvents for painting, propylene glycol (PG), propylene glycol propyl ether (PGPE), and dipropylene glycol propyl ether (DPGPE) improved the wetting of the particles in DI water. For the same amount of amphiphilic solvent added, PG delayed the least release; the characteristic release time was ~50 hr for PGPE and ~150 hr for DPGPE, suggesting a strong dependence of the diffusion on pore size. The bigger the block molecule in the pore, the more delayed release. The amount of the added solvent was also important for the delayed release. By comparison of the release profiles in aqueous solution of PG added 3 g and 10 g, respectively,

the release delay depended on the amount added. The more added PG, the more the delayed release.

The photoresponse of the modified particles has been checked for the release. The UV irradiation speeded up the release process as shown in Figure 9. The equilibration time in DI water was reduced from ~4 hr to ~1.5 hr for the
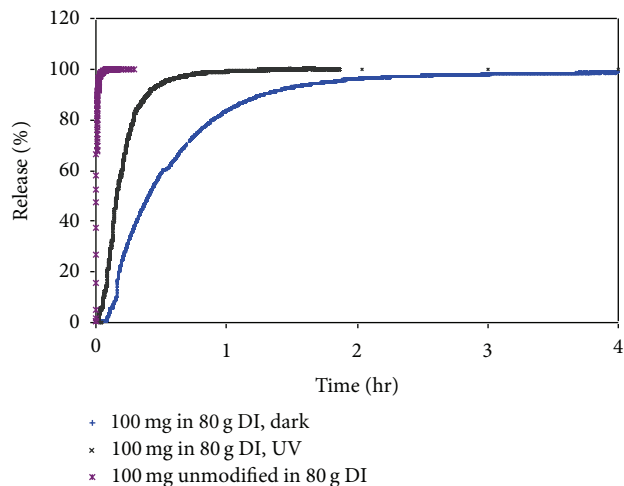
FIGURE 9: Photoresponsive release of azobenzene-modified NaCl/silica particles in DI water. The release from unmodified NaCl/silica particles is shown for comparison.
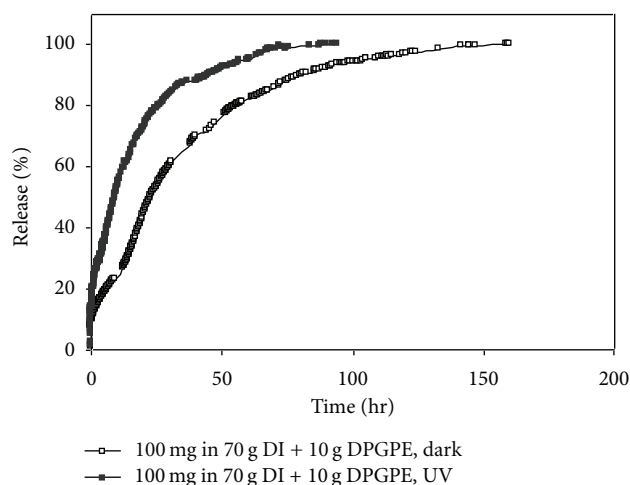

FIGURE 10: Photoresponsive release of azobenzene-modified NaCl/silica particles in DPGPE/water solution.

TABLE 2: NMR results for azobenzene-modified particle sample.

Si species	Shift (ppm)	Linewidth (Hz)	Integral (%)
T1	−51.0	500	5.15
T2	−57.6	500	3.89
T3	−65.1	500	1.29
Q2	−90.6	589	0.49
Q3	−99.7	690	11.75
Q4	−108.4	875	77.42

irradiation. As shown in Figure 10, when DPGPE was added, the equilibration time decreased from ~90–150 hr. The releases demonstrated a strong photoresponsive behavior for modified particles.

4. Conclusions

Azobenzene ligands have been successfully anchored uniformly to the pore surface. After the modification, the Q2 has reduced to only 0.49%, and the extend of condensation for Q species is as high as 96.45%, only 0.49% of Q2 existed, and the particles kept the ordered structures. The trans/cis transformation of the azobenzene moieties under UV irradiation realized the photocontrolled release. The addition of amphiphilic solvent into the release medium improved the wetting. However, the releases were delayed greatly after the addition of long block molecules. The delay depended on the amount and the size of the solvent added. This provides an extra external control of release in addition to UV irradiation. Long molecule solvents or polymers can be used as blocker to adjust the release behavior for a long-term controlled release.

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