Spectroscopic Probing of Adsorption of Uranyl to Uranyl-Imprinted Silica Sol−Gel Glass via Steady-State and Time-Resolved Fluorescence Measurement

Sheng Dai,*,† Y. S. Shin,‡ L. M. Toth,† and C. E. Barnes‡

Chemical Technology Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6181, and Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Steady-state and time-resolved fluorescence spectroscopic methods have been demonstrated to be very informative tools to analyze the microstructure variation induced by the imprinting technique. The structural information obtained provides the rationale for the enhanced uranyl-adsorption capacity and selectivity by the uranyl-imprinted sol−gel glasses.

Introduction

Fluorescence techniques have been widely used to probe surface characteristics of inorganic solids and organic polymers.[1,2] Fluorescence signals from probe ions adsorbed or covalently bound to solid matrixes can reveal information about their local environment through changes in their photophysical properties such as fluorescence lifetime and emission spectra. For example, the emission-lifetime distribution of a probe ion or molecule adsorbed on an inorganic sorbent has been directly correlated to the heterogeneity of the material.[1a,b,h] A wide variety of solid matrixes have been investigated via these techniques,[1,2,7] including silica,[1a,b,c,2] reversed-phase silica,[1h] zeolites,[2] titania,[2] clay,[2] and semiconductors.[1f]

The uranyl ion exhibits strong fluorescence signals with long emission lifetimes which are sensitive to both the local environment of the ion and its mobility.[3] For these reasons, the uranyl ion is an ideal, in situ photophysics probe for the investigation of the binding of this ion to a surface. Recent studies in our laboratories with sol−gel matrixes imprinted with uranyl ions (UO_2^{2+}) have shown enhanced selectivity and capacity toward uranyl separations.[4] In the present work, fluorescence techniques are used to investigate the variations in the surface microstructure of sol−gel matrixes induced by imprinting techniques. Ultimately we seek to relate models for the surface microstructure of imprinted matrixes to their macroscopic properties such as selective ion binding when competitive ions are present. Understanding these relationships is an essential engineering requirement in the preparation of new materials with tailored properties.

Imprinting methods based on the template approach have been used in cross-linked polymers[5−7] as well as in silica gels[9] to prepare polymeric supports possessing solid-state organized structures. Usually, imprinting processes (Scheme 1) involve three steps: (a) selection of target molecules as templates; (b) incorporation of the templates into rigid solid networks; (c) removal of the templates leaving cavities that later "recognize" or selectively bind the template or target molecule. The imprint cavity is produced by the template which is present during the formation of the solid matrix. After the templating species is removed from the polymer, a predetermined arrangement of ligands and a tailored binding pocket remains. Imprinted materials thus prepared have been shown to combine the binding ability of specifically chosen functional groups or ligands for

SCHEME 1: Imprinting Process via a Template (T)
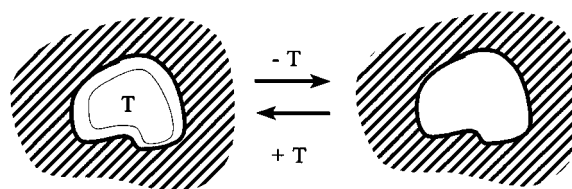
target substrates, with shape and size characteristics of cavities imprinted into a rigid polymer matrix by a template. Such materials are observed to selectively bind target substrates with high affinity and thus have many applications in the areas of separation science and catalysis. Imprinted organic polymers have been used to resolve racemates[6] and separate mixtures of metal cations.[7]

In imprinting technologies, it is of critical importance to be able to define in detail the properties of the imprinted cavity. These properties include defining the size and shape of the cavity as well as the type and number and functional groups involved in binding target ions. Furthermore, the distribution of templated cavities in the solid matrix must also be known. Previous studies of imprinted materials have relied on indirect measures to characterize the properties of imprinted cavities. No simple spectroscopic techniques have been developed which directly probe the surface microstructures induced by imprinting.

The solid-state silica network used to create imprints of UO_2^{2+} was prepared by the sol−gel process.[9] The sol−gel process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and condensation of tetraalkyl orthosilicates. Little or no heating is required, and consequently the gel can be doped or templated with molecules whose poor thermal stabilities preclude their incorporation in traditional high-temperature silica glasses.[10] Such molecules become entrapped in the growing covalent silica network rather than being chemically bound to the inorganic matrix.

Experimental Section

The instrumentation and procedures used for the measurement of both steady-state luminescence spectra and lifetimes have been described previously.[11,12a] The 337 nm line of a pulsed nitrogen laser (pulse duration = 5 ns) was used as the excitation source in these studies. Luminescence decay times were analyzed using both the Kohlraush−Williams−Watts (KWW) model and direct numerical inverse Laplace transform. The CurveFit program in SigmaPlot (Jandel Industries Corp.) was employed to fit experimental decay curves to the KWW model,
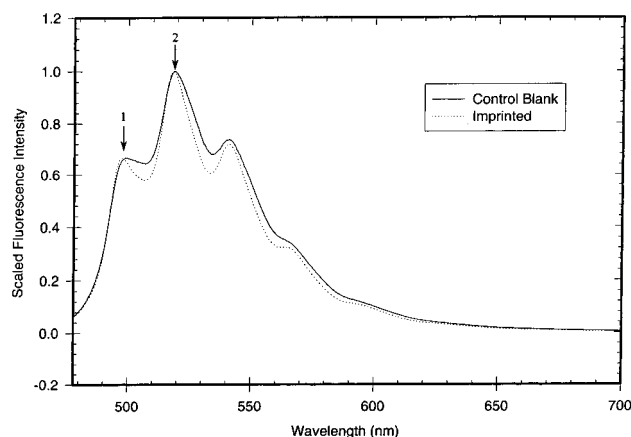
Figure 1. Comparison of experimental uranyl fluorescence spectra of reloaded control blank (solid line); and reloaded imprinted sample (doted line).

whereas the continuous model analysis program, CONTIN,[12] was used to conduct the numerical inversion of Fredholm and Volterra integral equations of the first kind (inverse Laplace transform). Solutions to the inverse Laplace transform were constrained to positive distribution coefficients. The line widths of emission spectra were obtained via CurveFit program in Grams/386 (Galactic Industries Corp.).

Literature procedures[13] were used to prepare uranyl-doped sol−gel glasses. In a typical run, 1 mL of an aqueous UO_2^{2+} solution (0.06 M $UO_2(NO_3)_2 \cdot 6H_2O$ dissolved in 2 N HNO_3) was mixed with 1 mL of tetramethyl orthosilicate (Aldrich Chemical Co., 99%), and 1 mL of methanol (Baker Chemical Co., HPLC grade). The final mixture was cured at the ambient temperature over a period of 4 weeks. Control blank samples were prepared in a similar manner except that no uranyl was added to the nitric acid solution.

It is well-known that the adsorption capability of silica-based sorbents toward UO_2^{2+} is very small below the pH of 2.[14] This characteristic in uranyl binding to silicates and highly porous microstructure of sol−gel glasses[9] prompted us to adopt acid washing as a method to efficiently remove the uranyl template ions from both surfaces and bulks of the glasses. Uranyl-free imprinted glasses were obtained by soaking the UO_2^{2+}-doped glasses in nitric acid (1 N) overnight. Control blank glasses were also washed with the identical nitric acid over the same period of time to ensure that both types of glasses had identical treatments of their surfaces. No UO_2^{2+} fluorescence signals could be observed in any of the washed samples.

Results and Discussion

Steady-State Fluorescence Studies of Uranyl Binding. Both imprinted and control blank glasses were immersed in identical aqueous solutions containing dissolved uranyl ion ($[UO_2^{2+}]$ 10^{-4} M, pH = 5.2) for reloading of uranyl ions. This reloading uranyl solution was prepared by titrating 10^{-4} M uranyl nitrate solution with tetrabutylammonium hydroxide (Fluka, 55−60% in water) to pH 5.2. Following overnight immersion, the samples were subsequently washed with hexane and dried in the air. This adsorption treatment gives rise to the concomitant appearance of fluorescence spectra attributable to uranyl complex species in both glasses (Figure 1a,b). Although the general spectral patterns and peak positions of spectra a and b are very similar, the line widths of the vibronic emission components are clearly different. Assuming the line shape of each vibronic emission line to be Gaussian, we can determine the corresponding line width through nonlinear least-squares fitting (CurveFit program in Grams/386). The line widths of
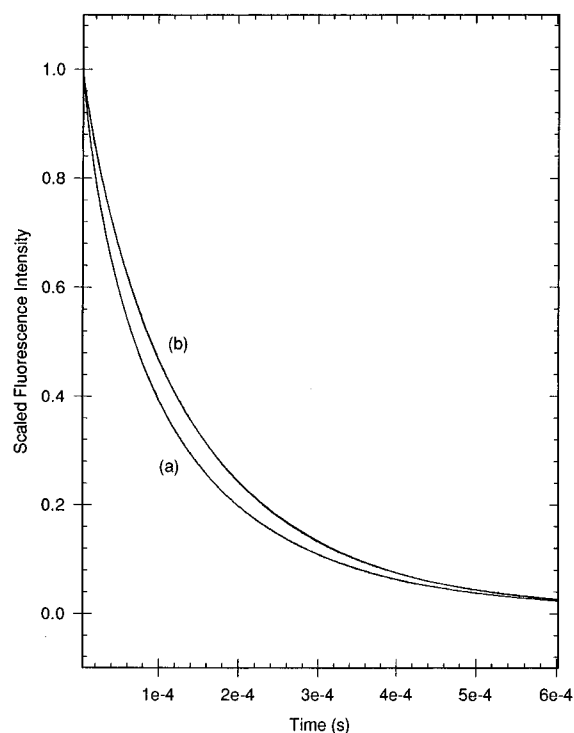

Figure 2. Comparison of experimental uranyl fluorescence decays (solid line) of (a) reloaded control blank and (b) reloaded imprinted sample with those obtained by fitting to KWW model (dotted line) and inverse Laplace transform (dashed line). All experimental and fitting decay curves are superimposed well with each other so that they cannot be easily distinguished from the figure.

TABLE 1: Line Widths of Two Main Vibronic Emission Peaks Obtained via Nonlinear Least-Squares Fitting

sample	line width (peak 1) (cm^{-1})	line width (peak 2) (cm^{-1})
imprinted	539	467
control	566	475

two main peaks obtained via nonlinear least-squares fitting (marked 1, 2 in Figure 1) are listed in Table 1. As seen qualitatively from Figure 1 and quantitatively from Table 1, the line widths of the vibronic emission lines corresponding to the imprinted sample are systematically smaller than those of the control blank. Wirth and Hahn[16] have pointed out before that the spectroscopic line width of an optical probe can be correlated with the shape selectivity of separation sorbents. This assertion was originally based on an intuitive argument that solutes having shapes incompatible with those of the solvation site would result in inhomogeneous broadening of the spectral line width through various interactions. Later, Wirth[15b] developed a physical model for this phenomenon by showing that structural order is a necessary condition for shape selectivity. Following the argument of Wirth,[15] we can attribute the narrower line widths of the emission lines for the reloaded imprinted sample to the shape-selective binding of uranyl ion in cavities produced by imprinting. In contrast, the adsorption of uranyl ion on the control blank would entail no shape selectivity, accordingly having broader line widths. The adsorption site of the imprinted material is more ordered and homogeneous than that of the control blank.
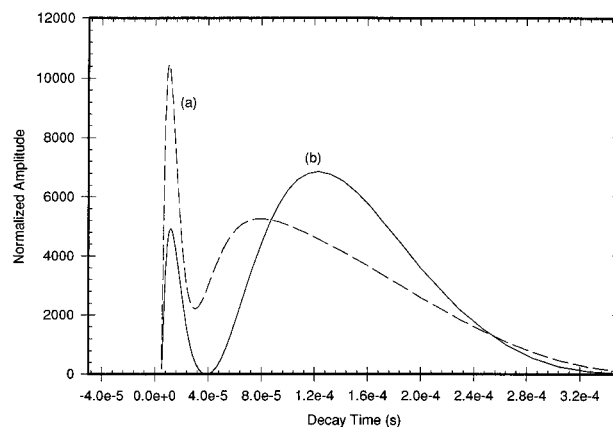
Fluorescence Lifetime Studies of Uranyl Binding. Fluorescence decay profiles of imprinted and control glass samples are shown in Figure 2. The two decay curves were measured at the maximum emission wavelength (518 nm). To avoid problems caused by noise associated with photon-counting statistics,[1a,11] 20 000 decay traces were acquired for each sample

109, 575. (e) Leung, L. K.; Komplin, N. J.; Ellis, A. B.; Tabatabaie, N. *J. Phys. Chem.* **1991**, *95*, 5918. (f) Heimer, T. A.; Meyer, G. J. *J. Lumin.* **1996**, *70*, 468. (g) Alivisatos, A. P.; Arndt, M. F.; Efrima, S.; Waldeck, D. H.; Harris, C. B. *J. Chem. Phys.* **1987**, *86*, 6540. (h) Huang, X.; Kovaleski, J. M.; Wirth, M. J. *Anal. Chem.* **1996**, *68*, 4119.

(2) (a) Thomas, J. K.; *Chem. Rev.* **1993**, *93*, 301. (b) Castellano, F. N.; Meyer, G. J. *Prog. Inorg. Chem.* **1997**, *44*, 167.

(3) (a) Denning, R. G. Electronic Structure and Bonding in Actinyl Ions. *Struct. Bonding* **1992**, *79*, 216. (b) Rabinowith, E.; Belford, R. L.; *Spectroscopy and Photochemistry of Uranyl Compounds*; McMillan: New York, 1964.

(4) Dai, S.; Shin, Y. S.; Barnes, C. E.; Toth, L. M., to be submitted.

(5) For leading reviews, see: (a) Wulff, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1812. (b) K. J. Shea, *Trends Polym. Sci.* **1994**, *2*, 166. (c) Mosbach, K. *Trends Biochem. Sci.* **1994**, *19*, 9. (d) Sellergren, B.; Lepistö, M.; Mosbach, L. *J. Am. Chem. Soc.* **1988**, *110*, 5853. (e) Flam, F. *Science* **1994**, *263*, 1221. (f) Davis, M. E.; Katz, A.; Ahmad, W. R. *Chem. Mater.* **1996**, *8*, 1820.

(6) Wulff, G.; Schauhoff, S. *J. Org. Chem.* **1991**, *56*, 395.

(7) Kuchen, W.; Schram, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1695.

(8) (a) Morrison, J. L.; Worsley, M.; Shaw, D. R.; Hodgson, G. W. *Can. J. Chem.* **1959**, *37*, 1986. (b) Dickey, F. H.; *Proc. Natl. Acad. Sci. U.S.A.* **1949**, *59*, 1039. (c) Curtt, R.; Colombo, U. *J. Am. Chem. Soc.* **1952**, *74*, 3961. (d) Dickey, F. H. *J. Phys. Chem.* **1955**, *59*, 695. (e) Raman, N. K.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682.

(9) (a) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: New York, 1990. (b) Lev, O. *Analusis* **1992**, *20*, 543.

(10) . For recent reviews and reports, see: (a) Zink, J. I.; Valentine, J. S.; Dunn, B. *New J. Chem.* **1994**, *18*, 1109. (b) Dunn, B.; Zink, J. I. *J. Mater. Chem.* **1991**, *1*, 903. (c) Avnir, D. *Acc. Chem. Res* **1995**, *28*, 328. (d) Klein, L. C. *Annu. Rev. Mater. Sci.* **1993**, *23*, 437. (e) Dunbar, R. A.; Jordan, J. D.; Bright, F. V. *Anal. Chem.* **1996**, *68*, 604.

(11) Dai, S.; Xu, W.; Metcalf, D. H.; Toth, L. M. *Chem. Phys. Lett.* **1996**, *262*, 315.

(12) (a) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213. (b) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 227. (c) Bowers, J. S.; Prud'Home, R. K.; Farinato, R. S. *Comput. Chem.* **1992**, *16*, 249. (d) Marshall, D. B. *Anal. Chem.* **1989**, *61*, 660.

(13) . (a) Dai, S.; Metcalf, D. H.; Del Cul, G. D.; Toth, L. M. *Inorg. Chem.* **1996**, *35*, 7786. (b) Dai, S.; Sigman, M. E.; Burch, E. L. *Chem. Mater.* **1995**, *7*, 2054. (c) Xu, W.; Dai, S.; Toth, L. M.; Del Cul, G. D.; Peterson, J. R. *J. Phys. Chem.* **1995**, *99*, 4447. (d) Dai, S.; Compton, R. L.; Young, J. P.; Mamantov, G. *J. Am. Ceram. Soc.* **1992**, *75*, 2865.

(14) (a) Milonjic, S. K.; Boskovic, M. R.; Ceranic, T. S. *Sep. Sci. Tech.* **1992**, *27*, 1642. (b) Lieser, K. H.; Quandt-Klenk, S.; Thybusch, B. *Radiochim. Acta* **1992**, *57*, 45. (c) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177.

(15) (a) Wirth, M. J.; Hahn, D. A. *J. Phys. Chem.* **1987**, *91*, 3099. (b) Wirth, M. J. *J. Phys. Chem.* **1987**, *91*, 3926.

(16) Press, W. H.; Teukolsky, S. A.; Vettering, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN: the Art of Scientific Computing*, 2nd ed.; Cambridge University Press: New York, 1992; p 206.

(17) (a) Allsop, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Carassiti, V.; Traverso, O. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 342. (b) Pandey, K. K. *Indian J. Pure Appl. Phys.* **1991**, *29*, 362. (c) Wheeler, J.; Thomas, J. K. *J. Phys. Chem.* **1984**, *88*, 750. (d) Lopez, M.; Birch, D. J. S. *Analyst* **1996**, *121*, 905.

(18) (a) Eliet, V.; Bidoglio, G.; Omenetto, N.; Parma, L.; Grenthe, I. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2275. (b) Decambox, P.; Moulin, V.; Decaillon, J. G. *Anal. Chem.* **1995**, *67*, 348.