Spectroscopic Investigation of the Photochemistry of Uranyl-Doped Sol−Gel Glasses Immersed in Ethanol

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Uranyl ion (UO_2^{2+}) has been doped in silica glasses through a sol−gel process. The photochemistry of UO_2^{2+}-doped glasses immersed in ethanol solution has been investigated. Our experimental results indicate that UO_2^{2+} in this system can be photochemically converted to U(IV) species, and evidence is provided for the possible formation of U(IV) species via a subsequent chemical reduction of the intermediate UO_2^+ instead of the conventional bimolecular disproportionation reaction. The latter mechanism is known to be a dominant mechanism for the photochemical reactions in homogeneous solutions.

Introduction

The photochemistry of uranyl ion (UO_2^{2+}) in homogeneous solution media has been the focus of many publications.[1−3] Recently, Bakac, Espenson and co-workers investigated uranyl photochemistry in aqueous solutions, with emphasis on the autoxidation of the intermediate uranium(V).[3] Nonetheless, few reports concerning the interfacial photochemistry of uranyl ion in heterogeneous media have appeared, with the exception of the work by Suib and co-workers.[4] They have demonstrated that bulk photolysis of uranyl ion-exchanged zeolites in isopropyl alcohol leads to the formation of molecular hydrogen and acetone after an induction period of 10 min.[4] The photoassisted catalytic oxidation of 2-propanol to acetone and H_2 is sustained for periods of over 300 h. Here, we describe our initial studies of the photochemical reactions of uranyl in transparent silica glasses immersed in ethanol solution.

The uranyl-doped silica glasses were prepared by the sol−gel process.[5] This process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and condensation of tetraalkylorthosilicates. Little or no heating is required, and consequently the gel can be doped with molecules whose poor thermal stabilities preclude their incorporation in traditional high temperature silica glasses.[6−8] Such molecules become entrapped in the growing covalent silica network rather than being chemically bound to the inorganic matrix. The glasses are often transparent so that the guest molecule can be electronically excited with visible or UV light. Photochemical products may be easily followed by measurements of changes of UV−vis spectra with the irradiation time.

The photochemical reaction mechanism (Scheme 1) of uranyl complex species in aqueous solutions is known to involve the photoreduction of UO_2^{2+} to UO_2^+ by reductants, followed by the disproportionation of UO_2^+ to U(IV) species and UO_2^{2+}.[1,2] The latter reaction is thought to be a very fast bimolecular process involving collision of two UO_2^+ molecules. Thus, the intermediate UO_2^+ is usually very difficult to detect. In the case of the sol−gel glasses, however the mobility of the entrapped uranyl and photogenerated UO_2^+ complex molecules should be very limited. Hence, the possibility of the bimolecular disproportionation reaction for UO_2^+ molecules is very small. This may enhance the chance of isolating the intermediate UO_2^+ complex species so that its chemistry can be studied in more detail.

Experimental Section

Sample Preparation. Literature procedures[8] were used to prepare uranyl-doped sol−gel glasses. In a typical run, 1 mL of $UO_2(NO_3)_2\cdot 6H_2O$ aqueous solution (0.04 M) was mixed with 1 mL of tetramethylorthosilicate (Aldrich Chemical Co., 99%), and 1 mL of methanol (Baker Chemical Co., HPLC grade). The uranyl solution was prepared by dissolving $UO_2(NO_3)_2\cdot 6H_2O$ into 1 or 2 N HNO_3 solution. The final mixture was cured at the ambient temperature over a period of 2 weeks followed by heating at 100 °C for 1 day. Similar methods were employed to prepare silica glasses doped with U^{4+}. In this case, 1 mL of 0.02 M UCl_4 solution was used and the glass was cured under an inert atmosphere.

The pore size distribution and available surface area in the glasses is a function of the method of glass preparation and curing temperature. The typical pore radius for the sol−gel glass prepared according to the procedure described above has been previously determined by an Autosorb 1 (Quantachrom Corp.) gas sorption isotherm and found to be about 5.4 Å.[8b]

Luminescence and Lifetime Measurement. The excitation for the measurement of luminescence spectra from the glass was 465 nm line of a Spectra-Physics Model 165 argon ion laser. A fiberoptic superhead (Dillor) was used in both the excitation and collection of signals from samples. The emission was collected at 0° with respect to the excitation direction, and dispersed with a Spex 500M monochromator with a 150 nm groove/mm grating blazed at 655 nm. The dispersed radiation was detected using a CCD (Charge Coupled Device) detector (Spex System

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Scheme 1

$$UO_2^{2+} + e^- \xrightarrow{h\nu} UO_2^{+} \qquad \text{(A)}$$

$$2\,UO_2^{+} \longrightarrow UO_2^{2+} + U(IV) \qquad \text{(B)}$$

One) with a 1 in. CCD chip. The resolution limit of this system is determined by the dispersion of the grating, the focal length of the monochromator, and the pixel size of the CCD detector and is 1.2 nm. Entrance slit widths less than 0.8 nm provide this resolution. For low-temperature measurements, the sample was mounted to the one-piece copper optical mount of a ADF DE-202 closed-cycle helium refrigerator. The temperature changes from 15 to 300 K.

For the luminescence lifetime measurement, the 465 nm line from an argon ion laser was used as the excitation source. The laser was chopped with a mechanical chopper (Stanford Research Systems, SR 540). The luminescence from the sample was dispersed using a monochromator (Spex 1404), and detected by a photomultiplier tube (PMT by Hamamatsu R636). The signals from the PMT were passed through an amplifier discriminator (Advanced Research Instrument Corp. MF-100) and recorded by a multichannel scaler (EG&G ORTEC, A68-B1) system. The luminescence decay was analyzed using the Curve Fit program in SigmaPlot (Jandel Industries Corp.). The time resolution of this setup for lifetime measurement is about 2 μs.

Photochemical Experiment. Visible and near-IR spectra were measured by a Cary 14 scanning spectrophotometer. Spectral data were collected and stored by On-Line Instrument Systems (OLIS) for data acquisition interface. Sol−gel glass samples were immersed in the ethanol contained in a quartz cuvette (0.5 cm pathlength). The ethanol is in contact with the atmosphere. UV−visible spectra were taken in-situ during the photolysis of the sample by 457 nm line of an argon ion laser (Spectra-Physics Model 165, about 70 mW laser power on samples). This laser light was transmitted to the sample compartment of the UV−visible spectrometer via an optical fiber.[9] This experimental setup has no moving parts during the photochemical experiment and, consequently, accurate plots of the photo-product concentration vs the photolysis time can be obtained.

Data Analysis. All spectra were transferred to a PC computer for processing. All software was written in FORTRAN (Microsoft, V3.2). The Jacobi method was used to find eigenvalues and eigenvectors for covariance matrices (vide infra).

Factor Analysis.[10−12] The objective of factor analysis is to determine the number of factors, contributing to a set of spectral data. We shall consider an $m \times n$ spectral data matrix $D = [d_{ij}]$; here i labels are for the spectrum taken at the photolysis t_i and j labels are for wavelength, $\lambda_1, \lambda_2, ..., \lambda_n$. This matrix can be used to form a covariance matrix , which is defined as

$$H = D^t D \tag{1}$$

where D^t is the transpose of D. Factor analysis shows that the number (k) of independent factors corresponding to the spectral data is equal to the number of nonzero eigenvalues of the covariance matrix H. Actually, the calculated "zero" eigenvalues are not identically zero but have some small magnitudes due to round-off errors in calculation and noise in experimental spectral data.

The k-eigenvectors($\mathbf{V}_j$'S) corresponding to these k-nonzero eigenvalues can be used as a new basis to expand observed spectra ($\mathbf{D}_i$):

$$D_i = \sum_{j=1}^{k} c_{ij} V_j \tag{2}$$

where c_{ij} is an expansion coefficient and determined by inner product ($\mathbf{D}_i$, $\mathbf{V}_j$). For a two-component system, the individual observed spectra can then be expressed as

$$D_i = c_{i1} V_1 + c_{i2} V_2$$

Through simple mathematical manipulation,[12b] it can be demonstrated that the coefficients c_{i1} and c_{i2} are related to one another by the following linear equation:

$$c_{i1} = a + b c_{i2} \tag{3}$$

a and b are constants. Equation 3 holds only for systems where the total concentration ($[c_1] + [c_2]$) of two components is invariant during experiments. Accordingly, the linear plot of c_{i1} vs c_{i2} can be used as a stringent test for the existence of a two component system.

Results and Discussions

Figure 1 shows the variation of the optical spectra during the photolysis of the sol−gel glass immersed in ethanol by a 457 nm line from an argon-ion laser. Since the experiment was conducted in the open air, the ethanol solution was saturated with O_2. Conducting the photochemical experiment in an Ar-saturated ethanol solution or in methanol solutions (saturated with O_2 or Ar) gave rise to the same photochemical phenomena. We found that yellow UO_2^{2+}-doped (0.04 M) glasses turn green in ethanol solutions upon photolysis. As seen from the Figure 1, a set of absorption bands around 650 nm appears with photolysis. These new optical bands agree well with the spectrum of the U(IV) complex species in ethanol solution as reported previously.[13] Ethanol is oxidized to acetaldehyde and other products. In order to further establish that the new bands can be attributed to those of the U(IV) species, we have prepared a U(IV)-doped sol−gel glass via an independent method, in which UCl_4 was chosen as the dopant. Figure 2 shows the comparison between the spectrum obtained via the photolysis of UO_2^{2+}-doped glasses and that of the U(IV)-doped glasses prepared by the independent method. Clearly, both the band positions and the spectral profiles of the two spectra match well. The small difference can be attributed to the different ligands surrounding the U(IV) species in the two systems. Therefore, the spectroscopic evidence and the green color of the glass indicate that UO_2^{2+} is photochemically converted to U(IV) species in the sol−gel glass matrix. *Complete photochemical conversion of uranyl into U(IV) species can be easily achieved with longer photolysis time.* As seen from Figure 1, there exist two isosbestic points in the spectra. One isosbestic point is around 420 nm while another is located around 445 nm. The existence of these isosbestic points in our spectra is consistent with a two-component system.[14]

Further support for a two-component system comes from the factor analysis of experimental data. As discussed in the previous section, the number of components can be more accurately determined by solving eigenvalue problems of the covariance matrix constructed from spectral data. In our case, the two major eigenvectors obtained from the diagonalization of the covariance matrix account for 99.81% of the total variance of the measured spectra. This is determined from the ratio of the nonzero eigenvalues of $\mathbf{D}^t\mathbf{D}$ to the trace of $\mathbf{D}^t\mathbf{D}$. With these two basis vectors, the expansion coefficients for our experi-

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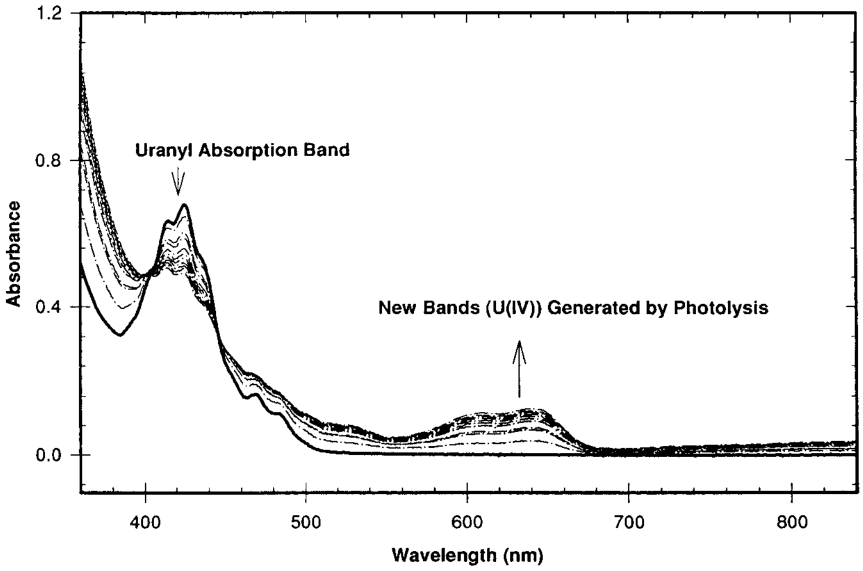

Figure 1. Spectral variation of a uranyl-doped glass under photolysis by an argon ion laser at 457 nm. The spectra were taken every 15 s. The solid curve corresponds to the uranyl spectrum before photolysis, while all dashed lines show spectra after photolysis.

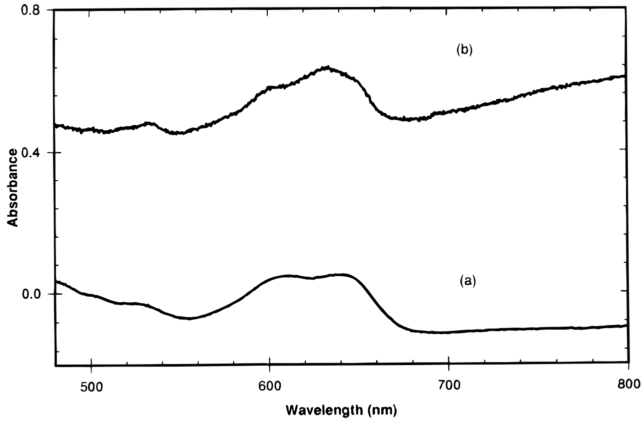

Figure 2. Comparison between UV−visible spectra of (a) the sol−gel glass doped uranium(IV) chloride and (b) that obtained from the photolysis of the sol−gel glass doped with uranyl.

mental absorption spectra are determined by the inner products.

$$c_{i1} = (V_1,D_i)$$

$$c_{i2} = (V_2,D_i)$$

The calculated points (c_{i1}, c_{i2}) are plotted in Figure 3 and approximately lie along a straight line. This is consistent with the behavior of a two-component system. Therefore, only photogenerated uranium(IV) complex species and unreacted UO_2^{2+} species were spectroscopically observed during photolysis. This establishment of a two-component system corresponding to the measured spectra allows us to follow the photogeneration rate of the uranium(IV) complex species since the photogenerated bands beyond 520 nm can be solely attributed to those of the uranium(IV) complex species. Figure 4 shows the growth of the uranium(IV) optical absorbance at 626 nm with photolysis time.

The facile photochemical reaction of uranyl to the uranium(IV) complex in the sol−gel glass is very surprising to us. If the photochemical reaction mechanism of uranyl complex species in sol−gel glasses is the same as that in the liquid solution phase, our results imply either that the photogenerated UO_2^+ complex species has a similar diffusion rate as that in liquid solutions or that uranyl ions in sol−gel glass matrices

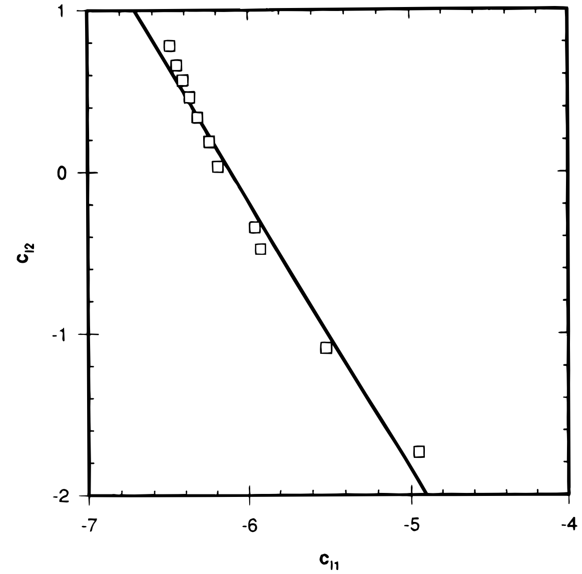

Figure 3. Plot of coefficients (c_{i1}, c_{i2}).

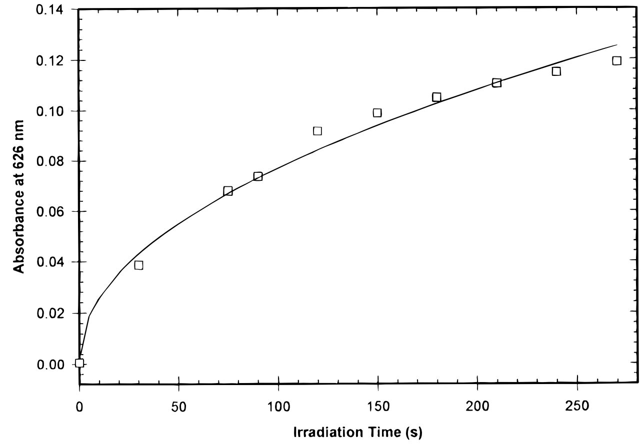

Figure 4. Plot of uranium(IV) absorbance at 626 nm vs the photolysis time.

exist in the form of polymeric species such as dimers and trimers so that the photogenerated UO_2^+ can be instantaneously converted to UO_2^{2+} and U(IV) species via disproportionation reaction (reaction B in Scheme 1). If UO_2^+ can freely move in

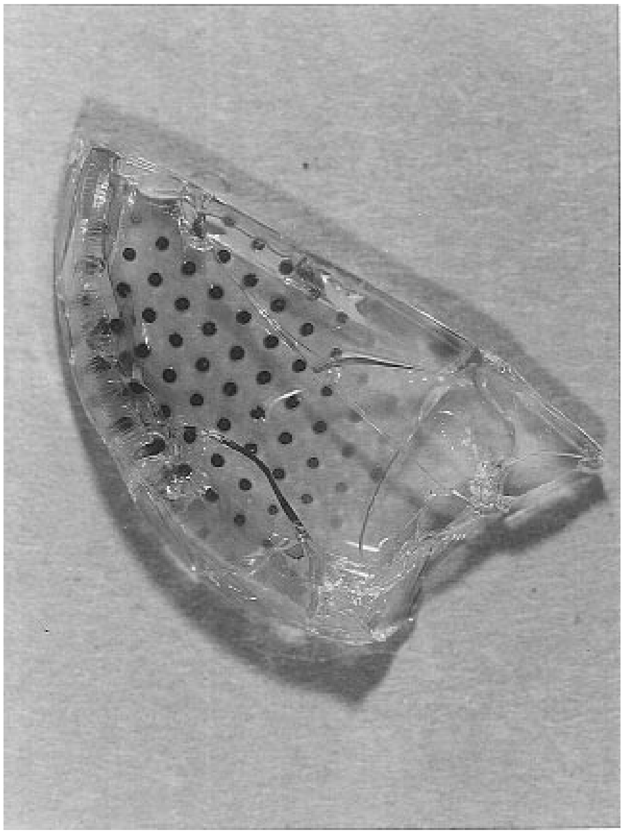

Figure 5. Picture of a U(+4)-imprinted uranyl glass.

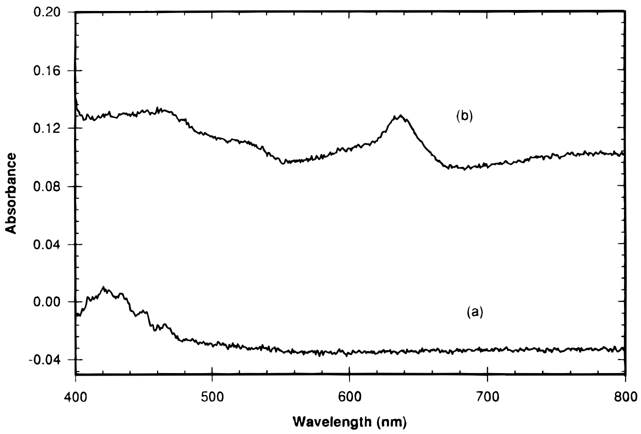

Figure 6. (a) Absorption spectrum of the glass containing 0.004 M uranyl before photolysis. (b) Absorption spectrum after 1 min photolysis.

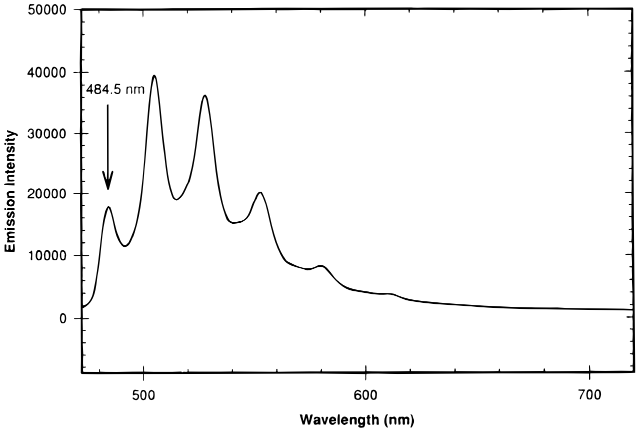

Figure 7. Fluorescence spectrum of a sol−gel glass containing 0.004 *m* uranyl.

sol−gel glasses, it can, of course, diffuse out of the glass matrix and into the ethanol solution. However, our experimental observations indicate that no leaching of uranyl, uranium(IV) species, and U(V) species into the ethanol solution occurs during the photochemical experiment which usually lasted for 1 or 2 days. Thus, this possibility may be ruled out. In order to visually demonstrate the immobility of the uranium photoproduct in sol−gel glasses, we masked the laser-beam (457 nm) with a 0.5 neutral density filter. An imprint of this patterned laser beam was generated in an uranyl-doped sol−gel glass through the photolysis of the uranyl-doped glass in ethanol solution by the laser. A photograph of one piece of the glasses produced in these experiments is shown in Figure 5. In the absence of air, the (green) dot pattern stays indefinitely in the glass. Since our sol−gel glasses are prepared by using the acid-catalyzed sol−gel process and cured at 100 °C under vacuum, both pore and cavity sizes are known to be very small, the possibility for one cavity to contain two or more molecular complex species is small.[5,8b] This possibility decreases with the concentration of the dopant, becoming negligible if a low concentration of the dopant (e.g., 0.002 M) is employed.

If the formation of polymeric species is responsible for the prompt photochemical reaction, decreasing the uranyl concentration in the sol−gel glass and the pH of the precursor sol−gel solution should eliminate the possibility for the formation of the polymeric uranyl species in our sol−gel glasses according to the respective equilibrium constants in the literature.[15] Therefore, the chance of the U(V)-disproportionation reaction is greatly reduced. Figure 6 shows spectral changes measured before and after photolyzing a sol−gel glass containing 0.002 M uranyl and prepared with the precursor solution having pH 0.05. Although all absorption bands are weak due to the low uranyl concentration, the bands corresponding to the U(IV) photochemical product can be easily seen from the spectrum after photolysis. This demonstrates that the photochemical reaction is concentration-independent, and therefore, the observed photochemical reaction is not dominated by the disproportionation reaction.

The additional evidence for the absence of the polymeric species as major species in sol−gel glasses can be found in fluorescence spectra of the sol−gel glasses doped with 0.01 M of the uranyl nitrate complex. Figure 7 gives a typical fluorescence spectrum of uranyl in the sol−gel glass. This spectrum was measured at 20 K. The origin of the fluorescence is located at 484.5 nm. It agrees well with the fluorescence origin of the monomeric uranyl nitrate complex in the literature,[16] since the Stokes origin of the polymeric species is known to be in the red to 485 nm (greater than 500 nm). The average spacing of vibronic bands is 835 cm^{-1}, which is very close to that of the monomeric uranyl nitrate complex in solutions and much greater than that of the dimeric species. A typical fluorescence decay curve is shown in Figure 8. This decay curve measured at 20 K can be reasonably approximated by a single exponential decay with an average lifetime equal to 3.9 $\times 10^{-4}$ s. Thus, we can conclude that the monomeric species is dominant in our sol−gel glasses. This conclusion is also consistent with the low pH (<1) of the starting uranyl solution. According to the dimmer/monomer equilibrium constant in

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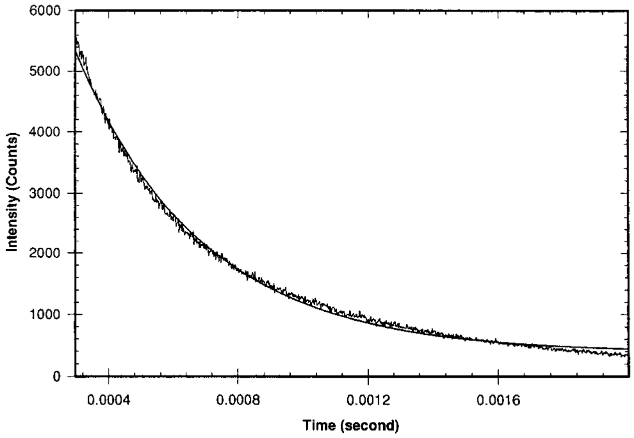

Figure 8. Fluorescence decay of a sol−gel glass containing 0.004 *m* uranyl, monitored at 500 nm.

aqueous solutions,[15] the dimeric concentration in this low pH starting solution is negligible.

The slow diffusion rate of uranium compounds and the absence of the dominant polymeric species in the sol−gel glass make it difficult to rationalize the prompt formation of U(IV) species through the conventional mechanism which involves the disproportionation reaction of UO_2^+. Therefore, we propose that the formation of the U(IV) compounds in our sol−gel glass may occur through a fast chemical reduction of the photogenerated UO_2^+. The high oxidation strength of UO_2^+ is well-known in the literature.[17,18] The electrode potential for the (UO_2^+/U^{4+}) couples is 0.55 V. Accordingly, UO_2^+ can act as a formal one-electron oxidant to a substrate that reacts as a reducing agent. A potential reducing agent is the $CH_3\dot{C}HOH$ radical, which is formed during photolysis of UO_2^{2+} in the presence of ethanol through a hydrogen abstraction reaction of CH_3CH_2OH by the excited state of UO_2^{2+}. Hence, one potential chemical reaction mechanism for the conversion of U(V) to U(IV) in the sol−gel glass may involve:

$$\mathrm{U(V)} + \mathrm{CH_3\dot{C}HOH} \rightarrow \mathrm{U(IV)} + \mathrm{CH_3CHO} + \mathrm{H^+}$$

Similar nondisproprotionation reactions of UO_2^+ are known in the literature.[1,17]

In conclusion, silica glasses doped with uranyl were prepared by the sol−gel technique. The interfacial photochemical reaction of the glasses immersed in ethanol has been investigated for the first time. U(IV) species were photochemically generated from UO_2^{2+}. Our photochemical experiments provide evidence for the possible formation of U(IV) species by a chemical reduction of UO_2^+ to U(IV) in the glasses, instead of the dominant conventional disproportionation reaction of UO_2^+. This is in contrast to the photochemical reaction of uranyl ion in homogeneous solution phases, where the formation of U(IV) is proposed to be only through the disproportionation reaction of UO_2^+. Therefore, our uranyl-doped sol−gel glasses can be a potential photocatalysis system for the oxidation of other organic compounds.

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