

Luminescence Properties of U(VI) Surface Species on Amorphous Silica

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1. Introduction

U(VI) (hexavalent uranium) in an aqueous solution is easily adsorbed onto solid surface under near neutral pH condition. Thus, the interactions of U(VI) with a variety of minerals have been widely studied to understand its migration behavior in groundwater system. The sorption characteristics of U(VI) onto SiO₂ surfaces were investigated at a molecular scale using several spectroscopic techniques, such as X-ray photoelectron spectroscopy, extended X-ray absorption fine structure spectroscopy, and time-resolved laser fluorescence spectroscopy (TRLFS). Among these techniques, TRLFS has received considerable attention because of its superior speciation sensitivity.

A lot of data on the luminescence characteristics (peak wavelengths in the spectrum and lifetimes of excited state) of U(VI) species adsorbed onto SiO₂ surface has been accumulated in literatures. However, the values of luminescence lifetimes of U(VI) surface species obtained by different groups differ significantly. Until now, the reason for these inconsistent luminescence lifetime values had not been clarified.

The objective of the present TRLFS study is to understand the origin of the inconsistent luminescence lifetime values of U(VI) species on SiO₂ surface reported in previous studies. We focus on the luminescence lifetimes of the U(VI) surface species which depend on the specific surface area (SSA) of SiO₂ samples and the incident laser pulse energy at UV wavelength. Other experimental parameters (aging effect of the sample and several instrumental parameters) are also examined.

2. Experimental Conditions

Four different SiO₂ powders are used in the present study. The first is a high-purity grade SiO₂ gel with a particle size of 40–63 μm (Sigma-Aldrich, 227196). The pore size of the SiO₂ gel is approximately 6 nm (0.8 cm³/g pore volume) with a SSA of approximately 477 m²/g. The second is hydrophilic fumed SiO₂ with a diameter of a few tens of nm (Evonik, Aerosil 200). It is a nonporous, amorphous material composed of spherical particles with a SSA of approximately 156 m²/g. The third is a spherical SiO₂ powder with a particle size of 1.5 μm and a SSA of approximately 2 m²/g (Alfa Aesar, L1698). The fourth is crystalline silica (α-quartz) with a particle size of approximately 5 μm and a SSA of approximately 7 m²/g (U.S. Silica, Min-U-Sil 5).

All the sample preparations are performed in an Ar-conditioned glove box with continuous stirring. The desired pH conditions are achieved by adding known amounts of 0.1 M NaOH or HClO₄ determined from pre-titration processes. Samples are further equilibrated in a rotary shaker for two or more days, after which the pH of the samples is measured using a glass combination electrode (OrionTM, Ross Ultra).

The luminescence intensities were measured using the kinetic mode of the intensified charge-coupled device with a gate delay time of 1 μs, a gate width of 1000 μs, and a gate delay step of 50 μs for the luminescence lifetime determination.

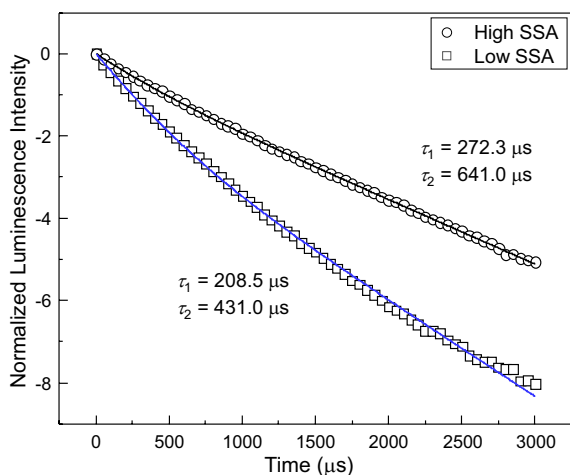


Fig. 1. Luminescence lifetimes measured from silica samples at pH 7.5. The luminescence lifetimes of the low SSA sample are shorter than those of the high SSA sample.

3. Results and Discussion

Fig. 1 shows luminescence lifetimes of U(VI) (concentration of 3.4 μM) measured from the low and high SSA SiO_2 samples at pH 7.5. The symbols depict the normalized luminescence intensities in the natural logarithmic scale. The solid lines represent the result of fitting the data to the double exponential decay equation. In Fig. 1, the luminescence lifetimes of the short- and long-lived species were determined to be $\tau_1 = 208.5$ and $\tau_2 = 431.0$ μs , respectively, for the low SSA sample (approximately 2 m^2/g). Whereas, the luminescence lifetimes were determined to be $\tau_1 = 272.3$ and $\tau_2 = 641.0$ μs , respectively, for the high SSA sample (approximately 477 m^2/g). The difference in the luminescence lifetime between the high and low SSA silica samples reflects that U(VI) species encounter a different distribution of surface sites.

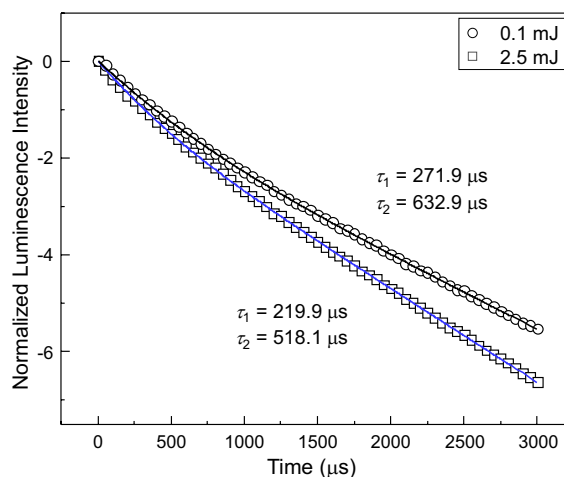


Fig. 2. Luminescence lifetimes measured from silica samples at pH 6.5. The luminescence lifetimes measured at 2.5 mJ are shorter than those measured at 0.1 mJ.

Fig. 2 shows luminescence lifetimes of the high SSA silica sample at pH 6.5 measured using the weak and strong laser pulse energies. The luminescence lifetimes measured at a strong laser pulse energy (2.5 mJ) are clearly observed to have become shortened. The reason of this phenomenon seems to be related to the laser-induced reaction such as a laser-induced desorption of adsorbates and the excited states annihilation.

4. Conclusion

We observed the differences in the luminescence characteristics (both the luminescence spectra and lifetimes) of the U(VI) surface species between the high and low SSA silica samples. It means that the distribution of surface sites has an important influence on luminescence characteristics of adsorbed U(VI) species. It is also observed that laser irradiation with a strong pulse energy at UV wavelength triggers a laser-induced reaction which results in the change of the luminescence characteristics. These phenomena can be pointed out as the origin of the inconsistent luminescence lifetime values reported in previous studies.