

Supplementary Materials

Surface Coverage- and Excitation Laser Wavelength- Dependent Luminescence Properties of U(VI) Species Adsorbed on Amorphous SiO₂

Euo Chang Jung^{1,*}, Yongheum Jo^{2,†}, Tae-Hyeong Kim¹, Hee-Kyung Kim¹, Hye-Ryun Cho¹,
Wansik Cha¹, Min Hoon Baik³ and Jong-Il Yun²

¹ Nuclear Chemistry Research Team, Korea Atomic Energy Research Institute, Daejeon 34057, Korea; thkim@kaeri.re.kr (T.-H.K.); hkim11@kaeri.re.kr (H.-K.K.); hrcho@kaeri.re.kr (H.-R.C.); wscha@kaeri.re.kr (W.C.)

² Department of Nuclear and Quantum Engineering, KAIST, Daejeon 34141, Korea; yongheum.jo@kit.edu (Y.I.); jiyun@kaist.ac.kr (J.-I.Y.)

³ Disposal Safety Evaluation Research Division, Korea Atomic Energy Research Institute, Daejeon 34057, Korea; mhbaik@kaeri.re.kr (M.H.B.)

* Correspondence: ecjung@kaeri.re.kr (E.C.J)

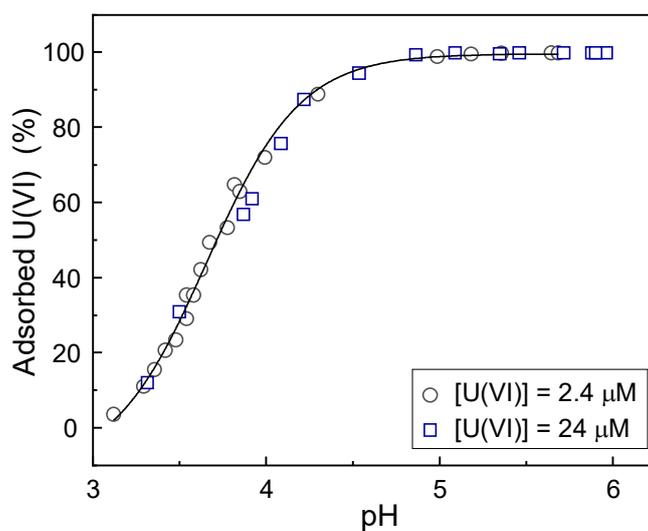
† Present Address. Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), 76344 Karlsruhe, Germany.

Table S1. Previously reported U(VI) surface species, thermodynamic surface complexation constants, and luminescence lifetimes. All measurements were conducted at room temperature. The Γ values were estimated using the [U(VI)], SiO₂ concentration (m/v), and SSA described in the references.

pH	Initial [U(VI)] Γ ($\mu\text{mol U/m}^2$) SSA	SiO ₂ type (diameter) m/v	Luminescence lifetime and complexation constant (relevant surface reaction)	Excitation laser wavelength (pulse energy)
3.5–8.0 ^a	100 μM 0.026 380 m^2/g	60H Merck (15 μm) 10 g/L	180 \pm 20 μs and $\log K^0 = -3.8 \pm 0.2$ ($\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} \leftrightarrow \equiv\text{SiO}_2\text{UO}_2 + 2\text{H}^+$) 400 \pm 30 μs and $\log K^0 = -20.0 \pm 0.1$ ($\equiv\text{Si}(\text{OH})_2 + 3\text{UO}_2^{2+} + 5\text{H}_2\text{O} \leftrightarrow \equiv\text{SiO}_2(\text{UO}_2)_3(\text{OH})_5 + 7\text{H}^+$)	355 and 430 nm (not reported)
3.7–8.87 ^b	0.1 and 1 μM 0.0006 and 0.006 169 m^2/g	Aerosil 200 (25 nm) 1 g/L	170 \pm 25 μs and $\log K = -4.9$ ($\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} \leftrightarrow \equiv\text{SiO}_2\text{UO}_2 + 2\text{H}^+$) 360 \pm 50 μs and $\log K = -10.5$ ($\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} + \text{H}_2\text{O} \leftrightarrow \equiv\text{SiO}_2\text{UO}_2\text{OH} + 3\text{H}^+$)	266 nm (4 mJ)
5 and 8 ^c	9 μM , 0.373 at pH 5 3.846 at pH 8 180 m^2/g	Aerosil 200 (25 nm) 0.134 g/L at pH 5 0.013 g/L at pH 8	227 μs for SiO-UO ₂ ⁺ 308 μs for SiO-(UO ₂) ₃ (OH) ₅	355 nm (not reported)
4.5–9 ^d	5 μM 0.040 505 m^2/g	Merck (size < 40 μm) 0.25 g/L	47 μs , 185 μs , 299 μs , > 450 μs	266 nm (0.5 mJ)
7–9 ^e	100 μM 0.036 559 m^2/g	Aldrich 637246 (5–15 nm) 5 g/L	159 \pm 23 μs for short-lived species 599 \pm 60 μs for long-lived species	266 nm (4 mJ)
3.1–7.9 ^f	3.4 μM , 0.007 and 0.021 156 and 477 m^2/g	Aerosil 200 (5–50 nm) Aldrich 227196 (40–63 μm) 1 g/L	233 \pm 16 μs for $\equiv\text{SiO}_2\text{UO}_2$ (pH 3.4–4.1) 296 \pm 17 μs for short-lived species (pH 7.0–7.6) 653 \pm 12 μs for long-lived species (pH 7.0–7.6)	266 nm (0.1 mJ)

^aRef. 13. ^bRef. 17. ^cRef. 18. ^dRef. 21. ^eRef. 24. ^fIn this study

(a)



(b)

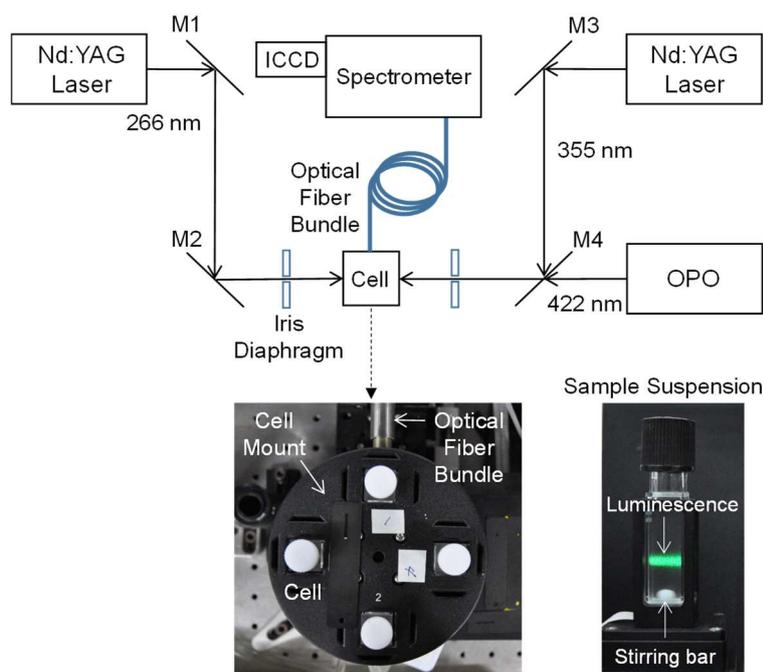


Figure S1. (a) Adsorption edge of U(VI)/SiO₂ system (sample No. 2). (b) The Schematic diagram of the experimental setup for TRLFS (M1 and M2: Dichroic mirror for 266 nm, M3 and M4: Dichroic mirror for 355 nm, M4 is mounted in the folding mirror mount). Iris diaphragms are installed on the travel path of the pulsed laser beam. Each laser system was used independently. The bottom left picture shows quartz cells, which are located inside the temperature-controlled cuvette holder. The bottom right picture represents the luminescence measured from the U(VI) adsorbed SiO₂ suspension. Stirring bar is placed at the bottom of the quartz cell.

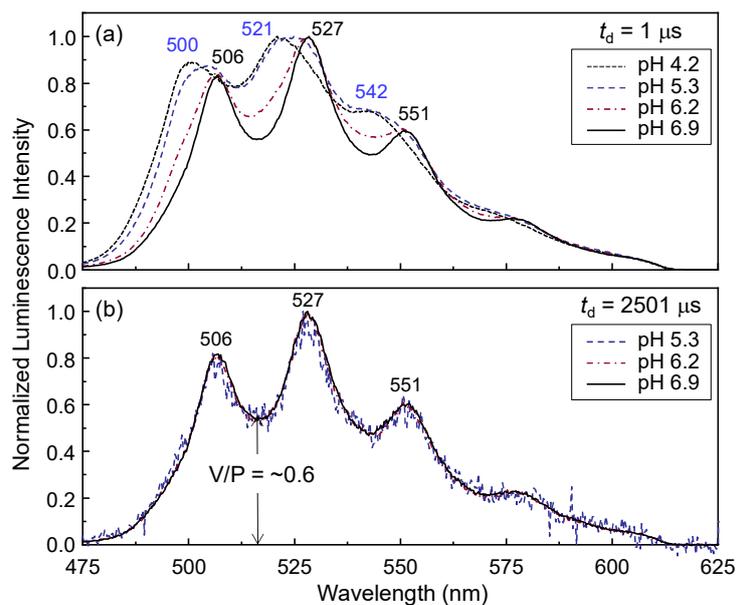


Figure S2. Normalized luminescence spectra of U(VI) adsorbed onto high SSA SiO₂ (sample No. 2, [U(VI)] = 3.4 μM, $m/v = 1.0$ g/L) under various pH conditions. The spectra were measured at $t_d = 1$ μs and 2501 μs. (a) The spectra measured at pH 5.3 and 6.2 demonstrate the change of dominant species from acidic to near-neutral pH conditions. (b) The almost identical spectral shapes show a V/P intensity ratio of approximately 0.6.

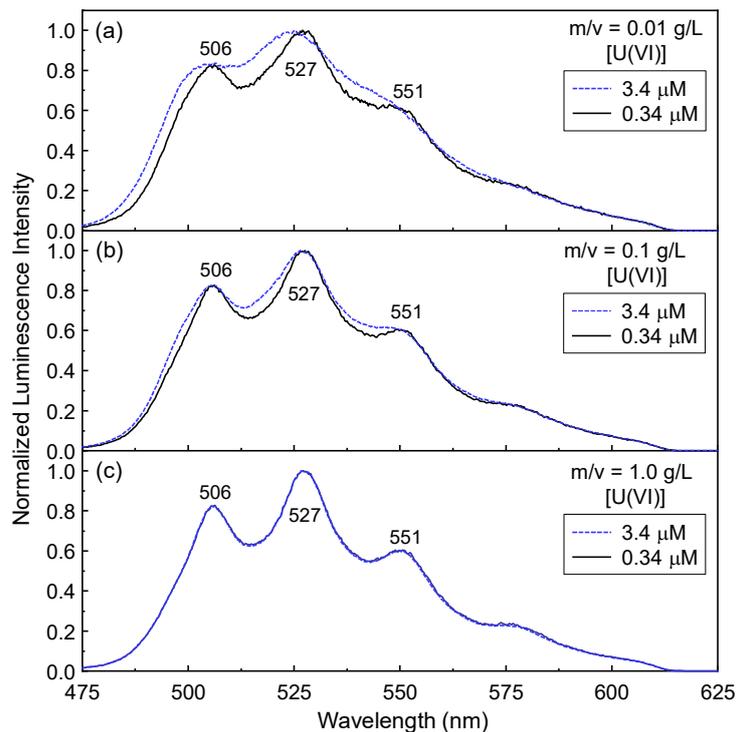


Figure S3. Normalized luminescence spectra derived from the data in Figure 2. Lower V/P intensity ratios are observed as [U(VI)] decreases from 3.4 to 0.34 μM with (a) $m/v = 0.01$ g/L and (b) $m/v = 0.1$ g/L. (c) The normalized luminescence spectra measured at $m/v = 1.0$ g/L show identical spectral shapes with the same V/P intensity ratio at [U(VI)] = 0.34 and 3.4 μM.

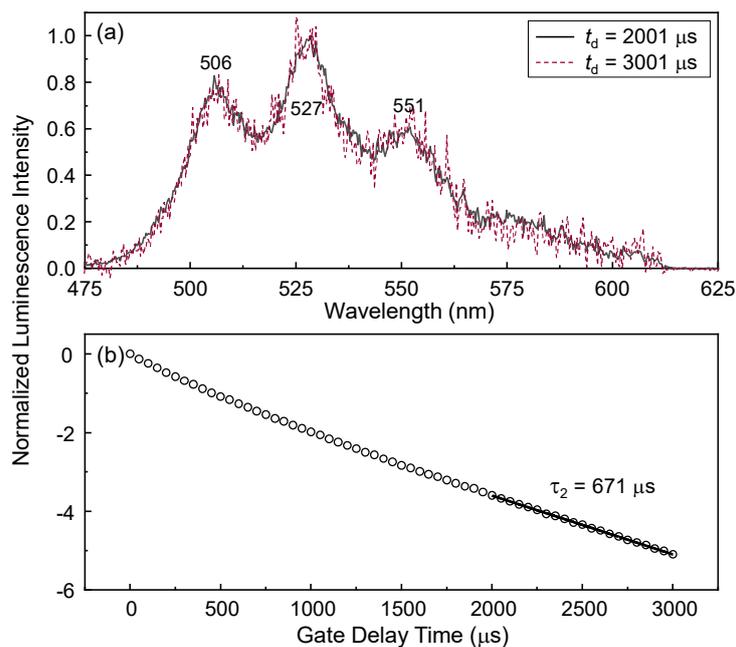


Figure S4. (a) For high SSA SiO_2 (sample No. 1, $[\text{U(VI)}] = 0.34 \mu\text{M}$, $m/v = 0.1 \text{ g/L}$, pH 7.5), the normalized luminescence spectra measured at $t_d = 2001$ and $3001 \mu\text{s}$ show almost identical spectral shapes. No significant changes in the peak wavelengths and spectral shapes were found in the kinetic luminescence spectra measured at various gate delay times in the range of 2001–3001 μs . (b) This result means that the luminescence lifetime of the species 2 can be determined by fitting the luminescence intensities on the natural logarithmic scale measured at $t_d = 2001$ – $3001 \mu\text{s}$ using linear regression. The luminescence lifetime of the long-lived species was determined to be $\tau_2 = 671 \mu\text{s}$ with a correlation coefficient of 0.9997.

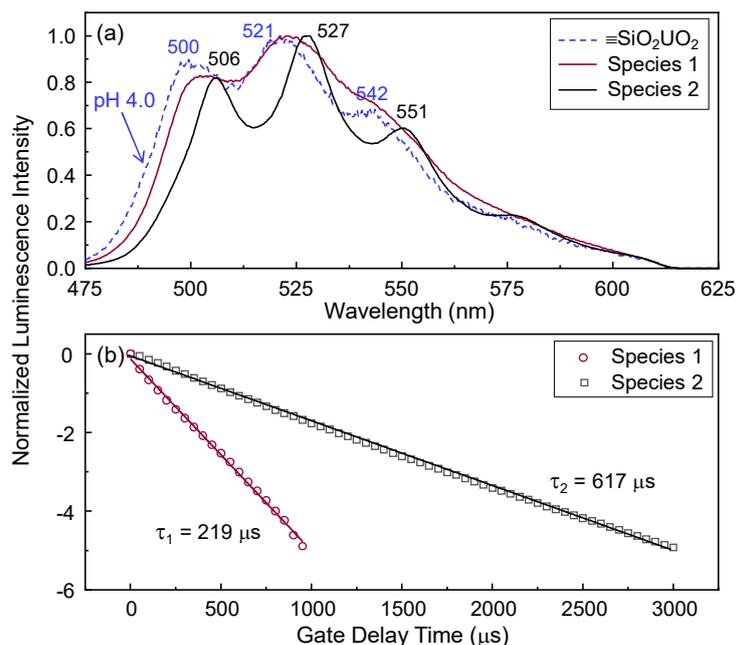


Figure S5. PARAFAC analysis obtained from the six spectra displayed in Figure 2. (a) The luminescence peak positions of species 1 measured at pH 7.5 do not exactly coincide with those of $\equiv\text{SiO}_2\text{UO}_2$. (b) The luminescence lifetimes of the decomposed spectra ($\tau_1 = 219$ and $\tau_2 = 617$ μs). However, these values obtained from the five datasets, excluding the highest Γ in Figure 2, changed to $\tau_1 = 306$ and $\tau_2 = 641$ μs , respectively (data not shown). This result also suggests that the luminescence characteristics of the U(VI) surface species depend on the Γ values.

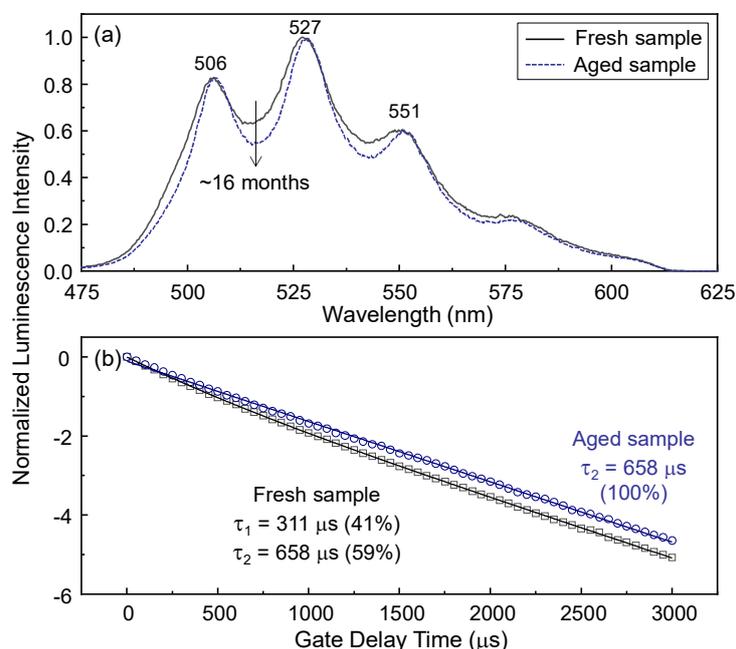


Figure S6. (a) The V/P intensity ratio of approximately 0.64 for fresh sample (sample No. 1, $[\text{U(VI)}] = 0.34$ μM , $m/v = 1.0$ g/L, pH 7.5) in the upper panel of Figure 2 changes to approximately 0.55 by 16 months of reaction. (b) The luminescence lifetime measurements demonstrate that the amounts of species 2 increases from 59% to 100% with increasing ageing time at the expense of species 1.

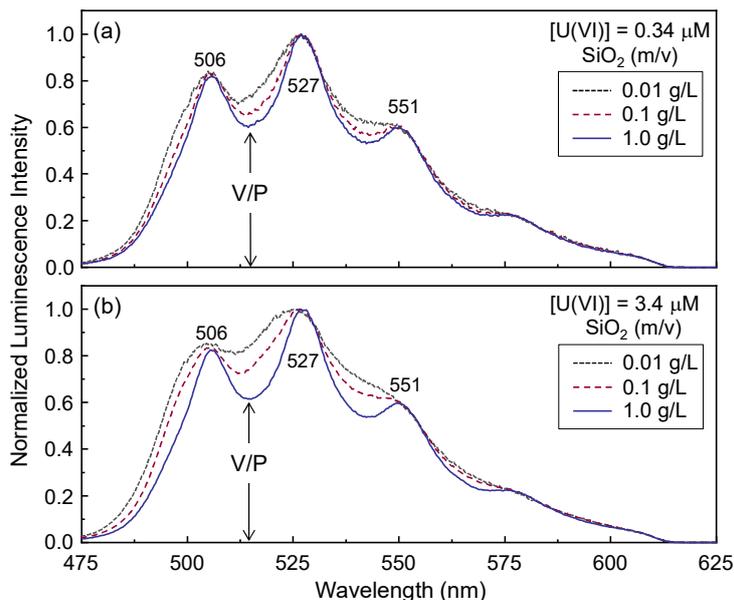


Figure S7. Normalized luminescence spectra of U(VI) adsorbed onto the high SSA SiO₂ (sample No. 2, pH 7.5) under various [U(VI)]/(*m/v*) ratios. The spectra were measured at $t_d = 1 \mu\text{s}$. (a) An increase in *m/v* at [U(VI)] = 0.34 μM leads to a lower V/P intensity ratio. (b) The change in the V/P intensity ratio becomes more pronounced at [U(VI)] = 3.4 μM compared with the change displayed in Figure S7(a).

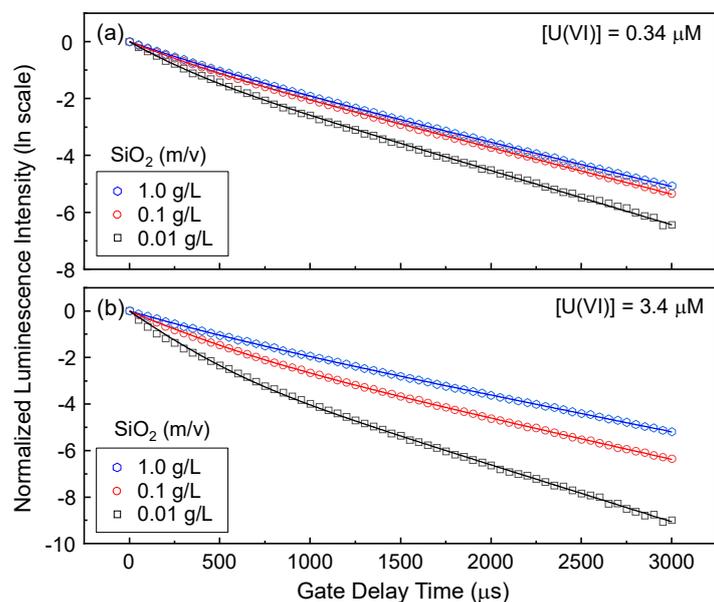


Figure S8. Luminescence lifetimes of U(VI) surface species measured from the samples used to obtain Figure S7. The kinetic mode of the ICCD was used with $t_d = 1\text{--}3001 \mu\text{s}$ and a gate delay step of 50 μs . The symbols represent the normalized luminescence intensity on the natural logarithmic scale for U(VI) surface species. The solid lines represent the fitting data obtained using Eq. (1). The lifetimes are listed in Table S2.

Table S2. Luminescence lifetimes and relative quantities of species 1 and 2 measured from the high SSA SiO₂ (sample No. 2, pH 7.5). These values were determined using the data shown in Figures S7 and S8. R² and RSS values are listed in the last column.

Samples		Γ ($\mu\text{mol U/m}^2$)	Species 1		Species 2		R ² (RSS)
[U(VI)] (μM)	m/v (g/L)		a	τ_1 (μs)	$1 - a$	τ_2 (μs)	
0.34	1.0	0.0007	0.397	321	0.603	654	0.99997 (0.0041)
3.4	1.0	0.0071	0.404	310	0.596	641	0.99992 (0.011)
0.34	0.1	0.0071	0.372	251	0.628	613	0.99988 (0.01665)
3.4	0.1	0.0712	0.675	254	0.325	571	0.9999 (0.0199)
0.34	0.01	0.0712	0.518	198	0.482	526	0.99948 (0.10252)
3.4	0.01	0.5702	0.824	171	0.176	410	0.99927 (0.27782)

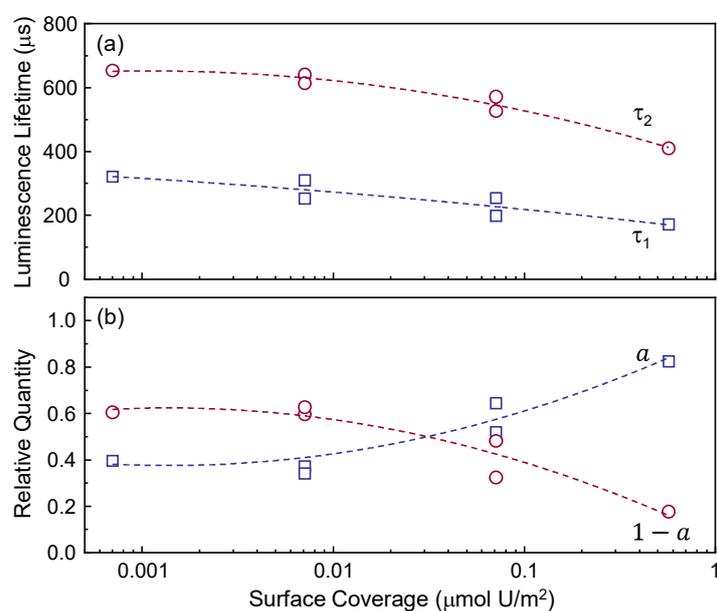


Figure S9. Luminescence lifetimes and relative quantities in Table S2 as a function of Γ . Blue rectangle and red circle represent the characteristics of species 1 and species 2, respectively. (a) The lifetimes of species 1 and 2 are denoted as τ_1 and τ_2 , respectively. (b) The relative contents of species 1 and 2 are denoted as a and $(1 - a)$, respectively. The dashed lines represent the results of fitting the data to the polynomial equation ($n = 2$) for easy observation of the increasing and decreasing behaviours of the data.

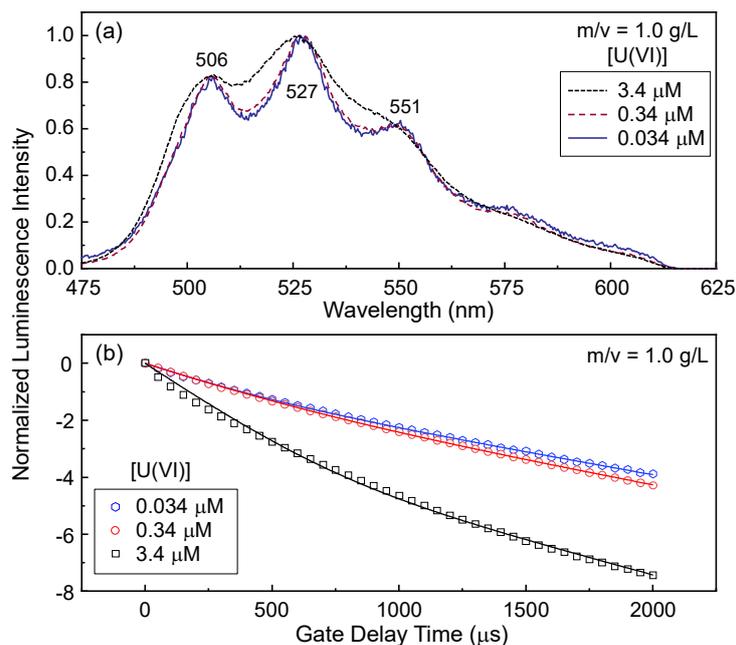


Figure S10. (a) Normalized luminescence spectra of U(VI) adsorbed onto the low SSA SiO₂ (sample No. 3, pH 7.5) under various [U(VI)]/(*m/v*) ratios. The spectra were measured at *t_d* = 1 μs. An increase in the [U(VI)] at *m/v* = 1.0 g/L leads to a higher V/P intensity ratio. (b) Luminescence lifetimes of U(VI) surface species measured from the samples used in Figure S10(a). The kinetic mode of the ICCD was used with *t_d* = 1–2001 μs and a gate delay step of 50 μs. The symbols represent the normalized luminescence intensity on the natural logarithmic scale for U(VI) surface species. The solid lines represent the fitting data calculated using Eq. (1). The lifetimes are listed in Table S3.

Table S3. Luminescence lifetimes and relative quantities of species 1 and 2 measured from the low SSA SiO₂ (sample No. 3, pH 7.5). These values were determined using the data shown in Figure S10. R² and RSS values are listed in the last column.

Samples		Γ (μmol U/m ²)	Species 1		Species 2		R ² (RSS)
[U(VI)] (μM)	<i>m/v</i> (g/L)		<i>a</i>	τ ₁ (μs)	1 - <i>a</i>	τ ₂ (μs)	
0.034	1.0	0.017	0.541	245	0.459	637	0.99975 (0.01311)
0.34	1.0	0.17	0.624	278	0.376	602	0.99981 (0.01178)
3.4	1.0	1.7	0.929	164	0.071	418	0.99745 (0.46938)

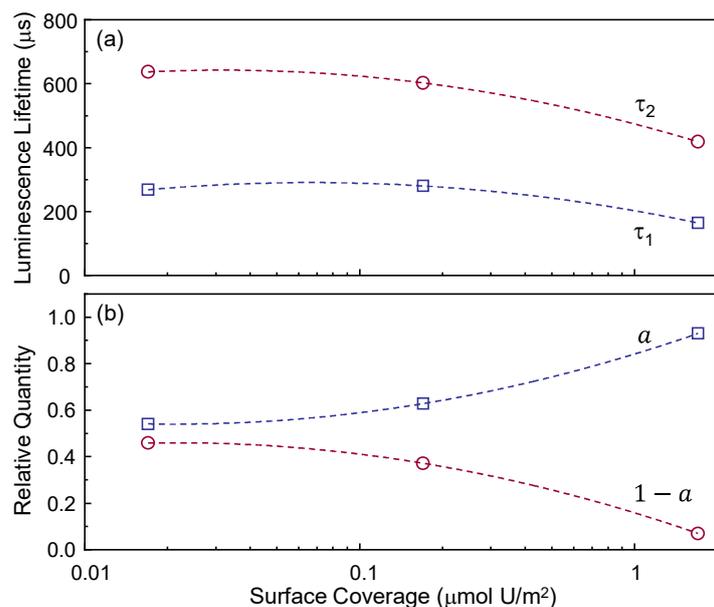


Figure S11. Luminescence lifetimes and relative quantities in Table S3 as a function of Γ . Blue rectangle and red circle represent the characteristics of species 1 and species 2, respectively. (a) The lifetimes of species 1 and 2 are denoted as τ_1 and τ_2 , respectively. (b) The relative quantities of species 1 and 2 are denoted as a and $(1 - a)$, respectively. The dashed lines represent the results of fitting the data to the polynomial equation ($n = 2$) for easy observation of the increasing and decreasing behaviours of the data.

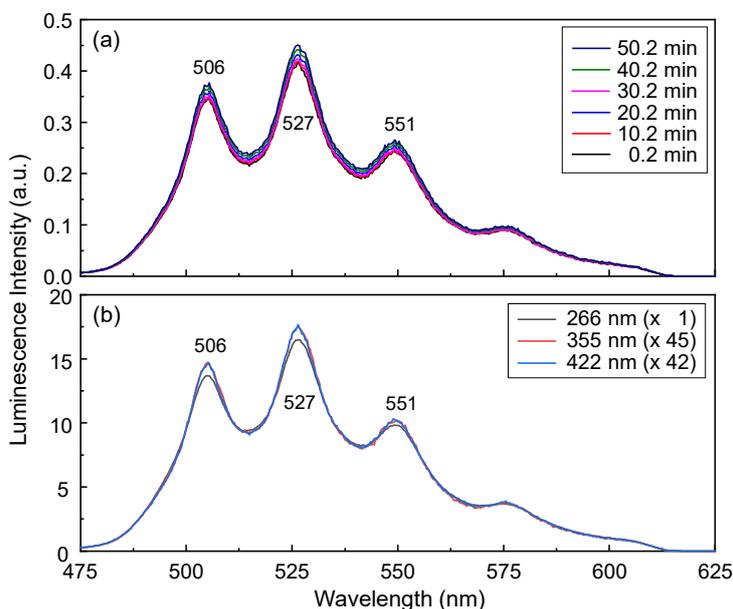


Figure S12. (a) There are no significant changes in either the luminescence intensities or spectral shapes during laser irradiation at $\lambda_{\text{ex}} = 422$ nm (laser pulse energy of 2.4 mJ) for the same SiO_2 sample used in Figure. 9. These results suggest that the laser-induced reaction does not occur at $\lambda_{\text{ex}} = 422$ nm. (b) The luminescence intensity at $\lambda_{\text{ex}} = 266$ nm is approximately 40 times stronger than the intensities measured at $\lambda_{\text{ex}} = 355$ and 422 nm at the same laser pulse energy of 2.4 mJ.