

## Effect of Ti(IV) Coating on the Adsorption of Eu(III) and U(VI) onto Silica in Aqueous Solutions

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### 1. Introduction

Fe(III) or Ti(IV) effects on the adsorption of Eu(III) onto silica surface in the aqueous solution were investigated in our previous published paper [1]. Next, the adsorption of  $\text{UO}_2^{2+}$  from an aqueous solution on Fe(III)- or Ti(IV)-coated silica was also examined to understand the radionuclide migration that occurs in groundwater and to compare the results with that of Eu(III).

Fe-modified silica gels were reported as an adsorbent for humic acids [2], and  $\text{TiO}_2$ -coated  $\text{SiO}_2$  synthesized by hydrolysis and condensation of various silicate and titanate precursors has been actively studied as photocatalysts owing to its photocatalytic and photovoltaic effects [3].

### 2. Experimental

Dry silica (particle size 40 to 63  $\mu\text{m}$ ; surface area 550  $\text{m}^2/\text{g}$ ) was dispersed in 3.7 M  $\text{HNO}_3$  for one day and washed with distilled water until the wet silica surface was neutral. Finally, the resulting silica was dried in an oven at 120°C for 6 h and stored in a capped bottle after cooling.

For the partial Fe(III) coating on the pretreated silica surface, a proper amount of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was added with stirring to each silica with pH adjusting to 4.5. The partially Fe(III)-coated silica was filtered, washed with a pH 4.5  $\text{HClO}_4$  solution and distilled water three times each, and dried at 120 °C for 6 h sequentially.

For the partial Ti(IV) coating on the pretreated silica surface, a certain amount of  $\text{Ti}(\text{O}i\text{Bu})_4$  was added with stirring to each silica. The partially Ti(IV)-coated silica was also filtered, washed with a  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{C}_6\text{H}_5\text{CH}_3$  (1:1) mixed solution three times, and dried in sequence at 120 °C for 6 h.

In each test, 500 mg of dissimilar Fe(III)- or Ti(IV)-coated silica was placed in 0.1 mM  $\text{Eu}_2\text{O}_3$  in 0.18 mM  $\text{HClO}_4$  and in 0.10 mM  $\text{UO}_2^{2+}$  in 0.16 mM  $\text{HClO}_4$  with a controlling ionic strength with 0.1 M  $\text{NaClO}_4$ . At this point, for the observation of a pH-dependent adsorption, 0.1 M  $\text{NaOH}$  under the  $\text{N}_2$  gas flow to eliminate the remaining  $\text{CO}_2$  in the solution, was properly added to each mixture. The pH went up to 8 for Eu(III) and 7 for U(VI) adsorption tests.

Conventional spectrofluorimetry and time-resolved laser fluorescence spectroscopy (TRLFS) of Eu(III) and U(VI) on Fe(III)- or Ti(IV)-coated silica were performed to observe luminescence from the surfaces of Fe(III)- or Ti(IV)-coated silica in aqueous solutions.

### 3. Results and discussion

It was confirmed from ultraviolet and visible (UV-vis) absorption spectra and inductively coupled plasma-atomic emission spectra (ICP-AES) analysis that 0, 2.05, 3.81, 7.38, 13.8, and 21.3  $\mu\text{mol/g}$  (Fe/silica) Fe-coated silica and 0, 16.1, 40.5, 63.9, 324 and 407  $\mu\text{mol/g}$  (Ti/silica) Ti-coated silica were obtained when appropriate amounts of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Ti}(\text{O}i\text{Bu})_4$  were added in each silica for the sample preparation [4].

It has been known that  $\equiv\text{Si-OH}$  in silica ( $\text{SiO}_2$ ) is dissociated into surface  $\equiv\text{Si-O}^-$  and free  $\text{H}^+$  at  $\text{pH} > 3$ , and as a result, the surface is negatively charged, which is appropriate to incorporate electron-deficient metals into silica surfaces. Here, Fe(III) or Ti(IV) was primarily fixed on the silica surface through the  $\equiv\text{Si-O-Fe}$  or  $\equiv\text{Si-O-Ti}$  structure. Next, hydrolyzed Eu-OH and U-OH is assumed to be adsorbed onto Fe(III)- or Ti(IV)-coated silica in aqueous Eu(III) and U(VI) solutions.

Ti(IV) coating enhanced both the Eu(III) and U(VI) adsorption onto the silica surfaces by increasing the amount of Ti(IV) on the surface, but Fe(III) coating on silica surfaces did not enhance adsorption of Eu(III) and U(VI) in the aqueous solutions.

However, as shown in Figs. 1 and 2, the luminescence intensity of Eu(III) at 394 nm excitation increased, while the luminescence intensity of U(VI) at 422 nm excitation decreased with an increased amount of coated Ti(IV). The shifting tendencies of the luminescence peaks with an increased amount of coated Ti(IV) were a little different from each other.

Moreover, the luminescence lifetime of Eu(III) at 616 nm increased and U(VI) at 520 nm decreased on partially Ti(IV)-coated silica with an increased amount of coated Ti(IV), as shown in Table I.

Details addressing their possible chemical interactions and the estimated speciation of Eu(III) or U(VI) complexes on Ti(IV)-coated silica will be discussed based on the luminescence spectra and luminescence lifetime data.

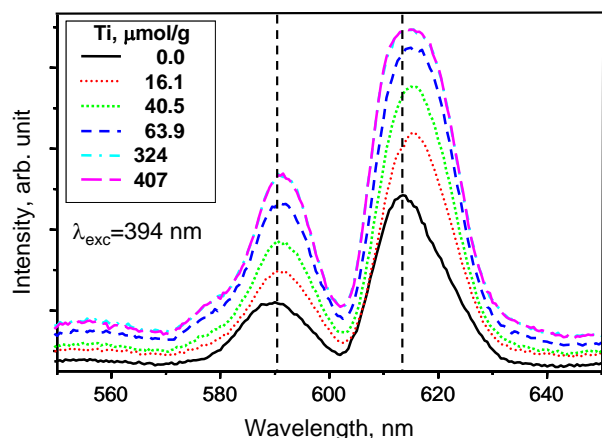


Fig. 1. Luminescence spectra ( $\lambda_{exc} = 394$  nm) of Eu(III) on partially Ti(IV)-coated silica according to the amount of coated Ti(IV) at pH 5 (in 0.10 mM  $Eu_2O_3$  in 0.18 mM  $HClO_4$ ) [1].

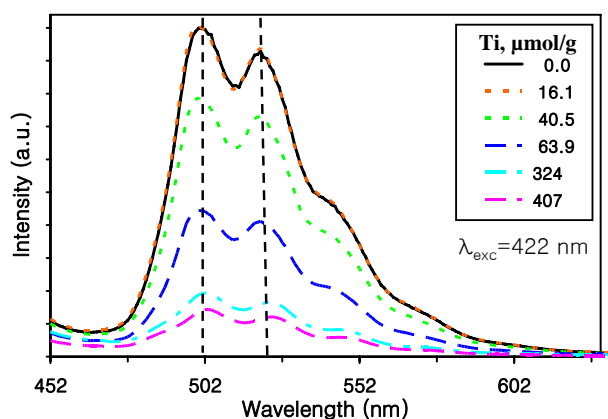


Fig. 2. Luminescence spectra ( $\lambda_{exc} = 422$  nm) of U(VI) on partially Ti(IV)-coated silica according to the amount of coated Ti(IV) at pH 5 (in 0.10 mM  $UO_2^{2+}$  in 0.16 mM  $HClO_4$ ) [4].

Table I. Comparison of luminescence lifetime of Eu(III) at 616 nm and U(VI) at 520 nm on partially Ti(IV)-coated silica according to the amount of coated Ti(IV)

Ti/silica ( $\mu\text{mol/g}$ )	Eu(III) lifetime ( $\mu\text{s}$ )	Ti/silica ( $\mu\text{mol/g}$ )	U(VI) lifetime ( $\mu\text{s}$ )
0.0	228.3	0.0	104.2
16.1	299.4	16.1	63.3
40.5	287.6	40.5	61.7
63.9	293.6	63.9	42.4
324	292.7	324	29.2
407	313.9	407	24.4

#### 4. Summary

Ti(IV) coating on silica showed different tendencies in luminescence intensity and luminescence lifetime with an increased amount of coated Ti(IV), in Eu(III) and U(VI) aqueous solutions. The surface-reaction

mechanisms and speciation of Eu(III) or U(VI) complexes onto Ti(IV)-coated silica in an aqueous solution will be discussed.

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