doi:10.1246/cl.2011.1381
Published on the web November 26, 2011

# Temperature-swing Microfluidic Separation of Uranyl Ions Using Thermoresponsive Copolymer Brushes

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This paper reports a novel temperature-swing microfluidic separation method. The selective adsorption–desorption of uranyl ($UO_2^{2+}$) ions could be realized by swelling–shrinking of a thermoresponsive copolymer brush, which was constructed with poly(*N*-isopropylacrylamide) (NIPAAm) and vinylpyrrolidone (VP) ligand, onto a microchannel surface. We clarified that the hydrophilic–hydrophobic transition temperature of the copolymer brush was about 35 °C and that the selectively for $UO_2^{2+}$ ions was 92%.

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Highly efficient separation and determination techniques of actinoides and lanthanoides have been strongly desired in various fields of chemical analyses, e.g., recovery of the valuable metals from seawater or waste solutions, preconcentration of trace amounts of the radionuclides for nuclear medicine, and so on.[1–3] Recently, micro- or nanofluidics have gained much attention as effective techniques.[4,5] The extraction of uranyl ($UO_2^{2+}$) ions or lanthanoides have already been performed by controlling liquid–liquid flows in 100 µm-sized microchannels, and their superior performances invoking high speed (a few min) and small reagent volume (ca. 100 µL) rather than bulk-scale methods have been verified.[6–8] However, since the microflows in microchannels are often unstable and difficult to control, they are still insufficient to separate mutually actinoides and lanthanoides having similar physicochemical properties.

Therefore, in the present study, we aim to establish a simple microfluidic separation concept, Temperature-swing microfluidic separation, for actinoides and lanthanoides. As shown in Figure 1, only $UO_2^{2+}$ ions can be adsorbed on a swelling thermoresponsive poly(*N*-isopropylacrylamide) (NIPAAm) copolymer with vinylpyrrolidone (VP) ligand, called poly(NIPAAm-*co*-VP), at ambient temperatures, but desorbed with increasing temperatures from the surface because of shrinking of the copolymer. In this case, the NIPAAm and VP are expected to act as the temperature-swing function and the ion selective function, respectively.[9–11]

The synthesis of poly(NIPAAm-*co*-VP) was performed by UV copolymerization as shown in Figure 2. A fused-silica substrate was modified by hydrophobic aminopropyltriethoxysilane (APTES) at 80 °C and 2 h under vacuum conditions. The APTES-modified substrate was immersed into dichloromethane ($CH_2Cl_2$) solution containing 4,4′-azobis(4-cyanovaleric acid chloride) (AIBN) photoinitiator. After the remaining $CH_2Cl_2$ solution was removed, the mixed solution of isopropylacrylamide (IPAAm) and vinylpyrrolidone (VP) monomers (molar ratio = 50:1) was sandwiched between two surfaces, and UV light (365 nm) was exposed to the surface at 10 min. As a result, poly(NIPAAm-*co*-VP) copolymer membrane could be synthesized onto the surface.

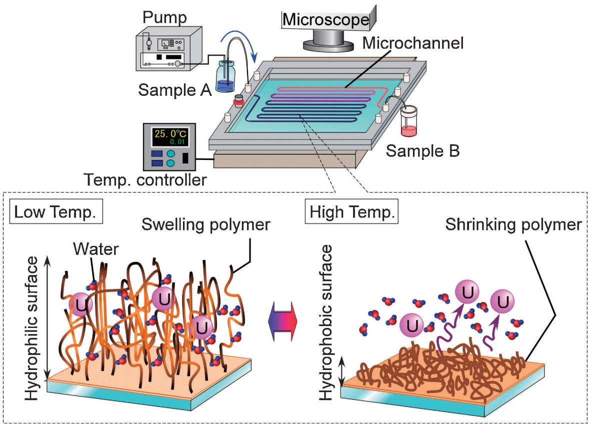

**Figure 1.** Concept of temperature-swing separation of $UO_2^{2+}$ ion on surfaces using a microfluidic control system.

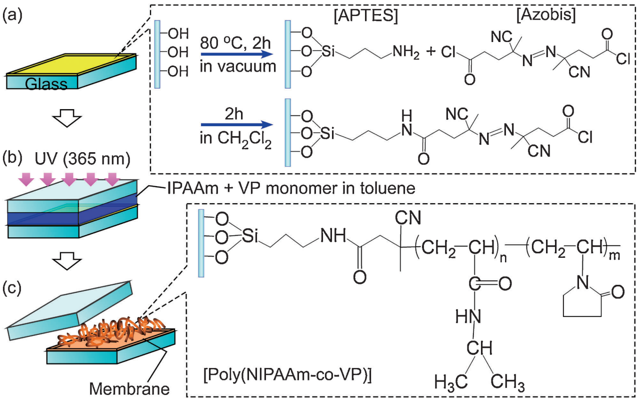

**Figure 2.** Synthesis scheme of poly(NIPAAm-*co*-VP) copolymer surface; (a) modification of initiator, (b) coating of monomer solutions and UV irradiation, and (c) copolymerization.

In order to examine the temperature-responsiveness of the synthesized poly(NIPAAm-*co*-VP) surface, the temperature dependence of contact angles for the poly(NIPAAm-*co*-VP) surface was measured using a contact angle meter (DropMaster500; Kyowa Interface Science, Saitama, Japan). As shown in Figure 3, the substrate at 25 °C showed slightly hydrophilic properties of about 30°, while the contact angles of the substrate were found to increase drastically with increasing

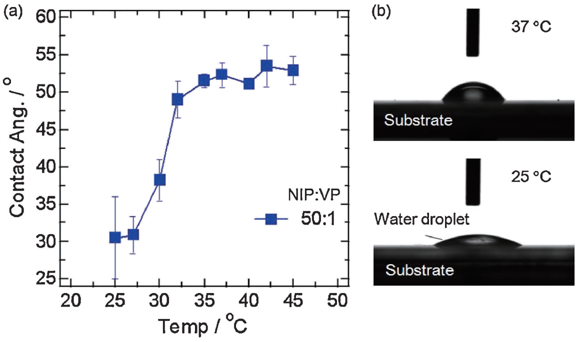

**Figure 3.** (a) Temperature-dependence of contact angles, (b) microscopic views of contact angels of water on poly(NIPAAm-*co*-VP) surface at 25 and 37 °C.

temperatures. When the temperatures increased to 35 °C, the contact angles of the substrate became about 55°, and the substrate could be converted to a hydrophobic surface. The results indicate that the synthesized poly(NIPAAm-*co*-VP) surface enabled hydrophilic–hydrophobic transition below and above 35 °C.

The adsorption–desorption properties of the poly(NIPAAm-*co*-VP) surface were examined according to the following procedures. Initial solution was prepared by 10 mM nitric acid solution containing strontium ($Sr^{2+}$), cerium ($Ce^{3+}$), europium ($Eu^{3+}$), and $UO_2^{2+}$ ions, and these concentration ratios were adjusted to Sr:Eu:Ce:U = 1:1:1:1 (called Sample A). The Sample A solution was dropped on the poly(NIPAAm-*co*-VP) substrate, and retained at 25 °C for 10 min. Since the poly(NIPAAm-*co*-VP) should be swelling, only $UO_2^{2+}$ ions are expected to be adsorbed on the surface. After the remaining Sample A solution was removed from the substrate, pure water was dropped on the surface. When the temperature increased up to 40 °C, the adsorbed $UO_2^{2+}$ ions would be desorbed from the surface in the water. Such solution (called Sample B) was recovered, and their ion concentrations were measured by induced-coupled-plasma atomic emission spectrometry (ICP-AES; Perkin-Elmer, Optima 3000). Figure 4 shows the bar graphs of relative concentration ratios for Samples A and B. The concentration of Sr was normalized as 1.0. We found that the concentration ratios of Sr, Eu, Ce, and U changed from 1:1:1:1 for Sample A to 1:18:7:176 for Sample B. The result indicated that the adsorption–desorption of $UO_2^{2+}$ ions on the poly(NIPAAm-*co*-VP) surfaces succeeded using only temperature-swing and that the selectively for $UO_2^{2+}$ ions became 92%.

In order to confirm whether the $UO_2^{2+}$ ions are selectively absorbed and desorbed on the poly(NIPAAm-*co*-VP) surface, X-ray fluorescence spectra of the surfaces before and after temperature-swing were measured. The results showed that only U peaks were observed on the surface at 25 °C, while at 35 °C the U peaks disappeared from the surface. This fact indicates that the complete catch and release of $UO_2^{2+}$ ions can be realized on the poly(NIPAAm-*co*-VP) surface.

Furthermore, after the photoinitiator and monomer solutions were filled in a microchannel (width; 40 µm, depth; 8 µm) on a fused-silica microchip, the poly(NIPAAm-*co*-VP) was synthesized onto the microchannel by UV irradiation. The copolymer-modified microchannel was repeatedly washed with ultrapure water before use. The initial 10 mM Sample A solution containing $Sr^{2+}$ and $UO_2^{2+}$ (concentration ratio; Sr:U = 1:1) was introduced from the vial to the nonmodified and the copolymer-modified microchannels by pressurizing with an air-pressure pump (Figure 1). The temperature was kept at 25 °C. The Sample A solutions through their microchannels were recovered at the outlet as Sample B solutions, and the concentration ratios of $Sr^{2+}$ and $UO_2^{2+}$ ions in recovered Sample B were measured by ICP analysis. The results showed that the concentration ratio of $Sr^{2+}$ and $UO_2^{2+}$ ions was almost the same as Sample A for nonmodified microchannel but was reduced by 1:0.43 for copolymer-modified microchannel. Namely, about 60% $UO_2^{2+}$ ions could be selectively trapped on the poly(NIPAAm-*co*-VP) copolymers in the microchannel.

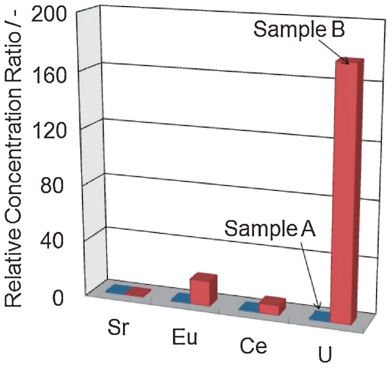

**Figure 4.** Relative concentration ratios of Sr, Eu, Ce, and U for Samples A and B.

Although the recovery efficiency of $UO_2^{2+}$ ions under dynamic microflow was still lower than that on a static surface, this poly(NIPAAm-*co*-VP) was found to act as effective $UO_2^{2+}$ adsorbent and to provide clear advantages for microfluidic separation.

This work was partially supported by “Funding Program for Next Generation World-Leading Researchers (NEXT Program)” from Japan Society for the Promotion of Science (JSPS).

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