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# Detection of Uranyl Ion Using Polymeric Membrane Containing Calix[6]arene Uranophile

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Abstract
To detect a low concentration of uranyl ions using a surface plasmon resonance (SPR) sensor system, a polymeric sensing membrane containing a water-soluble calix[6]arene was coated on the Au surface of a sensor chip. On the uranyl ion selective molecular-recognition function of the calix[6]arene, the constructed polymeric thin film as a sensing interface showed good sensitivity even in very low concentrations of uranyl ions ranging from $1.0 \times 10^{-5}$ M to $1.0 \times 10^{-12}$ M (0.1 M Tris-HCl Buffer, pH = 7.0).

Keywords uranyl ion; calix[6]arene; surface plasmon resonance

## INTRODUCTION

Owing to its great potential as an energy source, the selective and sensitive detection of uranium dissolved in water in form of the uranyl ion ($UO_2^{2+}$) has attracted the attention of many researchers.[1] Uranium dioxide is used in the preparation of fuel pellets for nuclear power reactors; moreover, small amounts of uranyl compounds as pollutants are dissolved in wastewater produced from dry and wet methods of available nuclear fuel preparation.[2] Low quantities ($1.0 \times 10^{-5} \sim 1.0 \times$

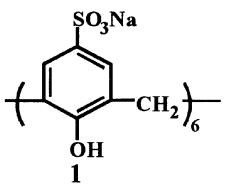
$10^{-3}$ M) of waste with weakly radioactive uranyl ions ($UO_2^{2+}$) produced in the preparation of nuclear fuel could lead to lethal environmental damage.[3] Therefore, it is indispensable that we develop an effective uranyl ion sensor with high sensitivity, good selectivity, and fast response time.

In this paper, the study of a new uranyl ion sensor system based on the resonance angle shift of SPR (Surface Resonance Plasmon) and the uranophile characteristics of a calix[6]arene is described.



## EXPERIMENTAL

Because a water soluble calix[6]arene derivative (**1**) is a well-known highly selective uranophile, we used **1** as a ionophore in this study (Figure 1).[4] Compound **1** was prepared using a procedure similar to that reported by Sinkai et. al [5]. In order to construct the $UO_2^{2+}$ ion-sensing membrane, it was immobilized according to the following procedure. The casting solution for a polymeric-sensing membrane for SPR measurement was composed of a PVC-PVAc-PVA matrix co-polymer (Poly(vinylchloride-*co*-vinylacetate-*co*-vinylalcohol), Aldrich chemical Co. Inc., M.W. = 27,000, 23.2 w/w %), plasticizer (DOP, dioctyl phtalate, Aldrich chemical Co. Inc., 51.2 w/w %), an anionic site ((NaTm($CF_3$)$_2$PB), Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate, Fluka, 6.8 w/w %), and the calix[6]arene (18.8 w/w %) in THF (Tetrahydrofuran, Junsei chemical Co. Ltd.). This solution was spin-coated (4500 rpm, 30 seconds) on the bare Au surface of an SPR sensor chip and then baked at 80°C in an oven for 30 minutes.




**1**

FIGURE 1 Calix[6]arene uranophile.

The incident angle modulating SPR sensor system based on the Kretschmann prism configuration for the uranyl ion detection and the structure of the sensor chip are shown in Figure 2 and Figure 3.[6] In the case of this SPR system, after surface plasmon resonance on the Au

surface, the beam reflected through the prism arrives at the photo detector (ANDO electric Co. Ltd., AQ1135E). The prism is rotated by X-Y-θ stage with a resolution of 0.004° (minimum resolution) to change the incident angle of the laser beam. The power intensities of the reflected laser beam according to resonance angle shifts were measured by varying concentrations of metal ions ($UO_2^{2+}$ = $1.0 \times 10^{-12} \sim 1.0 \times 10^{-5}$ M and $Li^+$, $Na^+$, $K^+$, $Cs^+$, $Mg^{2+}$, $Cu^{2+}$, $Zn^{2+}$ = $1.0 \times 10^{-12} \sim 1.0 \times 10^{-5}$ M in Tris-HCl, 0.1 M, pH = 7.0).

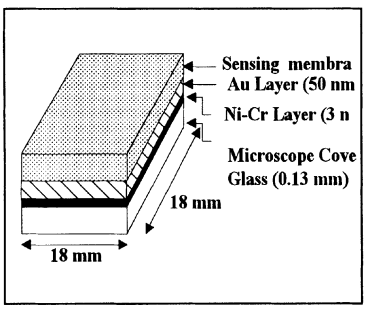



FIGURE 2 Structure of the sensor chip.

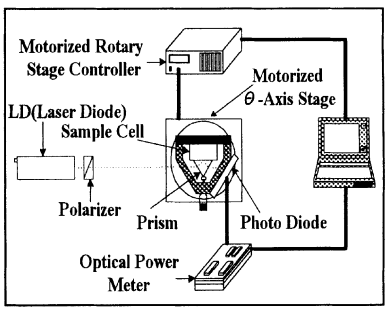



FIGURE 3 Schematic diagram of an incident angle modulating SPR sensor system.

## RESULTS AND DISCUSSION

As shown in Figures, 4 and 5, the difference of the resonance angle shift increased in accordance with the $UO_2^{2+}$ ion concentration. The response time was very quick and the sensitivity was about 0.09° per decade concentration of $UO_2^{2+}$ (from $1.0 \times 10^{-12}$ M to $1.0 \times 10^{-5}$ M). The sensing membrane system showed good selectivity even at the very low concentration of $UO_2^{2+}$ ion. Comparing these experimental results with general detection limits ($1.0 \times 10^{-5} \sim 1.0 \times 10^{-6}$ M) of conventional spectroscopic or electrode method about uranyl ion, it is possible to apply the system as a good method to overcome their detection limit.

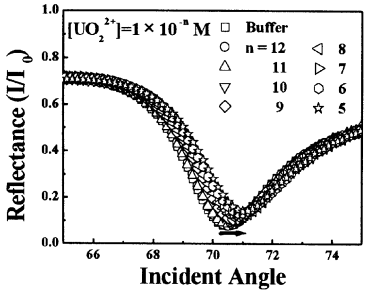



FIGURE 4 Resonance angle shifts according to different uranyl ion concentrations (0.1 M Tris-HCl Buffer, pH = 7.0).

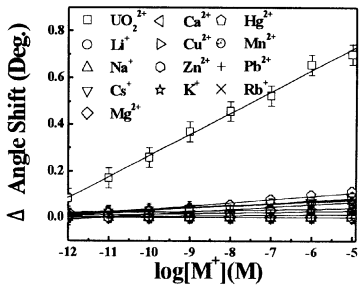



FIGURE 5 Resonance angle shifts to several kinds of metal ions using the sensing membrane (0.1 M Tris-HCl Buffer, pH = 7.0).

In conclusion, a recognition-functional molecular system with the sensitive SPR principle showed good $UO_2^{2+}$ ion detection ability. It is quite likely that these experimental results will be useful for the design of more simple and more precise uranyl ion sensors.

Acknowledgements

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