Sensors and Actuators B 134 (2008) 419–422

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Uranyl ion detection based on wavelength-resolved surface plasmon resonance spectroscopy

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ARTICLE INFO

Article history:
Received 10 September 2007
Received in revised form 1 May 2008
Accepted 16 May 2008
Available online 23 May 2008

Keywords:
Surface plasmon resonance
Uranyl ion
Calix[6]arene
White light source

ABSTRACT

Wavelength-resolved surface plasmon resonance (SPR) system was developed using white light source, which showed a high sensitivity in very low concentrations of uranyl ion ranging from 1.0×10^{-5} M to 1.0×10^{-12} M. The combination of wavelength-resolved SPR technique and careful construction of appropriate recognition film was an essential method for the development of more efficient sensor interface.

1. Introduction

Surface plasmon resonance (SPR) sensor is one of the generalized high-sensitive and selective sensing systems [1]. Traditional SPR biosensing devices are based on fixing a discrete excitation wavelength and measuring the angle of incident light [2,3]. The SPR reflected spectra are shown in terms of reflected light intensity *versus* angle of the incident light. In practice, the surface plasmons are excited by a convergent beam of monochromatic light, and the resonance angle is measured using a photodetector array. The best angular accuracy of this SPR biosensor is about 0.001°, which corresponds to a shift in optical wavelength of 0.6 nm, which makes its sensitivity to be limited [4]. Such an instrument is much more expensive than the one described here. In this study, the wavelength-resolved SPR is developed based on fixed incident angle and measuring resonance wavelength using a white light source.

In this paper, a novel SPR sensing system based on a wavelength shift using a white light source is reported. For demonstrating the performance of the novel sensing system, the calix[*n*]arene derivatives were immobilized to monitor uranyl ions. The sensing film was formed on the Au and characterized by SEM. The combine well constructed uranophile-containing film and wavelength-resolved SPR showed the stable and sensitive detection for uranyl ion sensing.

2. Experimental

2.1. Reagents and sample preparation

Poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol) and dioctyl phtalate were bought from Aldrich Chemical (Milwaukee, WI, USA). Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and uranyl acetate dihydrate were purchased from Fluka Chemi AG (Buchs SG, Schweiz). A stock solution of uranyl ion (1.0×10^{-3} M) was prepared in 0.1 M Tris–HCl buffer, pH 7.0. All solutions and buffers were prepared with deionized water using a Milli-Q Water System (≥18 MΩ cm).

The structure of calix[6]arene derivative used as the uranophile studied in this work is shown Fig. 1a. Compound **1** was prepared using a procedure similar to that reported by Shinkai et al. [5].

2.2. Preparation and characterization of sensor chip

A microscope cover glass (18 mm × 18 mm Matsunami, Japan) with gold layer was used as a substrate for the formation of UO_2^{2+} ion-sensing membrane. The gold film (thickness ≈ 50 nm) was deposited by the sputter coating system (E5000, Polaron Co., UK) after 3-nm nickel–chromium depositions on the cover glass. The

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doi:10.1016/j.snb.2008.05.017

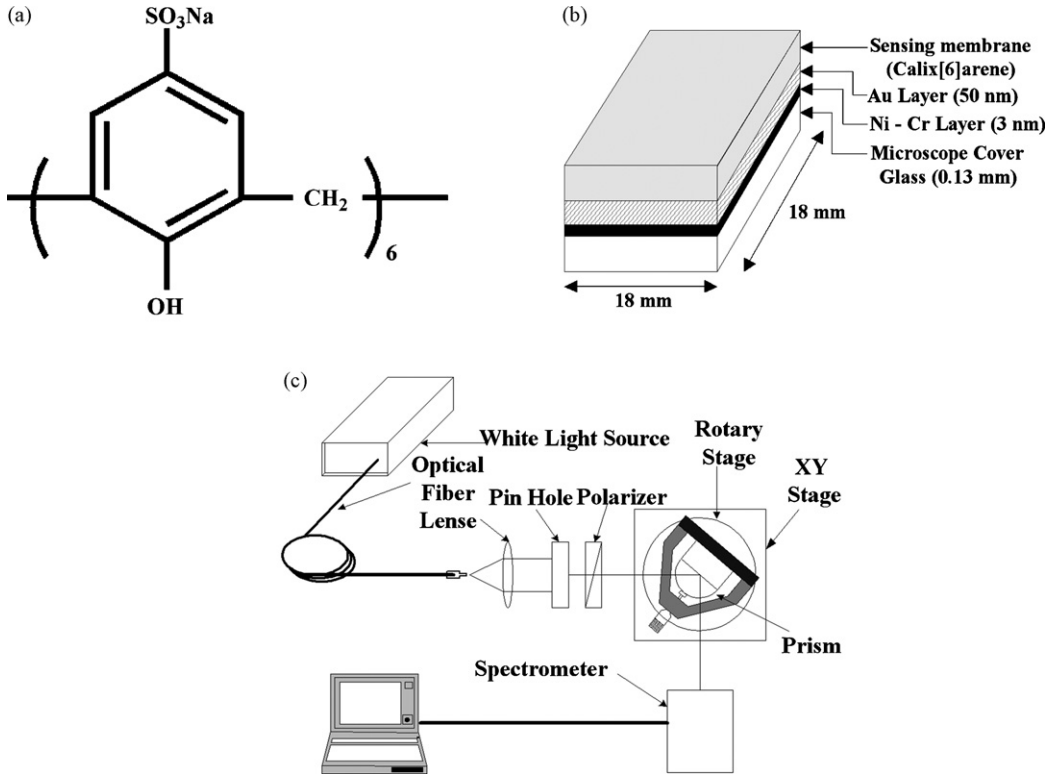

Fig. 1. (a) The molecular structure of calix[6]arene uranophile; (b) schematic diagram of the sensor chip; (c) schematic diagram of SPR system.

sputtered Au substrate was rinsed using distilled water, methanol and acetone, sequentially. Then, the gold chip was dried in a nitrogen stream softly and ready to use.

To construct the UO_2^{2+} ion-sensing membrane, it was immobilized according to the following procedure [6]. The casting solution for polymeric sensing membrane for SPR measurement was composed of PVC–PVAc–PVA matrix copolymer (poly(vinyl chloride-*co*-vinyl acetate-*co*-vinyl alcohol), MW = 27,000, 23.2 wt%), plasticizer (dioctyl phtalate (DOP), 51.2 wt%), anionic site (sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, 18.7 wt%), and calix[6]arene derivative (18.7 wt%) in tetrahydrofuran (THF). The mixed solution was spin-coated (4500 rpm) on the surface of Au and then the chip was baked in an oven at 80 °C for 30 min. The sensor chip consists of the cover glass with an Au layer, a Ni–Cr adhesion layer and a polymeric sensing membrane spin-coated on Au surface (Fig. 1b). The morphology of the polymer films was carried out by scanning electron microscopy (SEM) (Model: S-400, Hitachi).

2.3. Apparatus

The SPR spectroscopic measurements for the interactions between uranyl ions and the recognition film were performed by homemade wavelength-resolved SPR system based on the Kretshmann prism configuration (Fig. 1c) [7]. The white lamp was used as light source, which is much cheaper than the laser light source used in the traditional SPR. The lens is utilized to make the light from the source to be a parallel one. The parallel light is polarized by the polarizer. The incident angle into the prism varied with the motorized rotary stage and its controller (Suruga Seiki, D80, Shizuoka, Japan). The reflected intensity of light by the way of the polarizer and the prism is guided into a spectrophotometer (spectra view 2000, K-MAC Co., Korea) and is interfaced with a computer.

The incident angle is fixed at a suitable value to ensure the surface plasmon resonance phenomenon to occur. A smaller change in refractive index or layer thickness at the sensor surface would cause a clear wavelength shift of the resonant wavelength in SPR-reflected spectra. After rinsing with Tris–HCl buffer (0.1 M, pH 7.0), eight various uranyl ion solutions in a concentration range of 1.0×10^{-12} M to 1.0×10^{-5} M were injected into the cell from the lower one to higher one for 10 min and followed by rinsing with Tris–HCl buffer.

3. Results and discussion

3.1. Characterization of sensing membrane

Fig. 2 shows the SEM microphotograph of fracture surface of sensing membrane. The polymer film showed dense morphology of the fracture surface. The thickness of UO_2^{2+} ion-sensing membrane was identified to be about 11 nm using SEM measurement, which is consistent with the value (10.6 nm) calculated from SPR curve using Fresnel equation based on four-layer model (prism, gold, sensing membrane and environment) [8,9]. As a result of these measurements, the UO_2^{2+} ion-sensing membrane has uniform quality.

3.2. Uranyl ion sensing by wavelength-resolved SPR sensor system

To confirm the efficiency of wavelength-resolved SPR system, the relationship between incident angle and wavelength was invested. It was found that the SPR occurred with rapid reflectivity change at specific angle according to the increase of incident angle to wavelength alteration (Fig. 3). The dark part of the contour line represented that SPR angle shifted to lower one with increasing wavelength. These results indicated that the sensing membrane has an effective SPR-induced wavelength shift using a white light source.