Sensors and Actuators B 171–172 (2012) 287–293

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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

Surface plasmon resonance optical sensor for detection of Pb^{2+} based on immobilized p-tert-butylcalix[4]arene-tetrakis in chitosan thin film as an active layer

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ARTICLE INFO

Article history:
Received 18 September 2011
Received in revised form 18 March 2012
Accepted 23 March 2012
Available online 2 April 2012

Keywords:
Surface plasmon resonance
Optical sensor
Pb^{2+}
p-Tert-butylcalix[4]arene-tetrakis
Chitosan
Sensitive
Selective

ABSTRACT

Surface plasmon resonance (SPR) optical sensor, for sensitive and selective detection of Pb^{2+}, was developed in this study based on p-tert-butylcalix[4]arene-tetrakis (BCAT) immobilized in chitosan thin film as an active layer. Pb^{2+} can be detected by measuring the SPR signal when BCAT immobilized chitosan thin film is exposed to Pb^{2+} in aqueous solution. The BCAT immobilized chitosan thin film was coated on a gold layer by spin coating technique. The measurements were carried out for Pb^{2+} concentration ranging from 30 ppb to 5 ppm. A linear relationship between the shift of SPR angle and concentration of Pb^{2+} up to 1 ppm, with sensitivity of 0.045° ppm^{-1} has been observed. Pb^{2+} can also be selectively detected when present in mixtures of heavy metal ions containing Cu^{2+}, Hg^{2+}, Zn^{2+} and Mn^{2+} ions.

1. Introduction

Recently, the presence of lead in the environment has been a great concern because of its increased discharge and possible toxic effects to human [1]. The toxicity of lead had been studied extensively since it can induce a wide range of adverse effects in humans [2]. Pb^{2+} binds with the —SH group in enzymes or proteins causes inhibition of enzymes. Lead can also affect bone by interfering with metabolic and homeostatic mechanisms including parathyroid hormone, calcitonin, vitamin D and other hormones that influence calcium metabolism [3]. Lead substitutes for calcium in bones and hence affects osteoblasts, osteoclasts, chrondrocytes, osteoporosis and delays in fracture repair [4]. Acute lead poisoning may also cause severe damage in brain, kidney, liver, central nervous system, cardiovascular system, immune system, or even death [5–7]. For mild lead poisoning, it may cause premature birth, sore muscle, anaemia, headache and the victim may feel fatigued and irritable [8].

Due to its dangerous toxic effect to human, several methods for determining Pb^{2+} have been developed include atomic absorption spectroscopy [9–11], inductively coupled plasma mass spectroscopy [12–14], electrochemical impedance spectroscopy [15], voltammetry [16–19] and polarography [20]. However, these methods generally are expensive and mostly take a long measuring period. Therefore, recent analytical interest has focused on developing optical sensors, which have the advantages of size, cost-effectiveness, simple preparation of sample, fast measurement capability and no necessity of reference solution [21–23]. Surface plasmon resonance (SPR) spectroscopy, one of the optical sensors, has been developed in various configurations and formats for sensing of analytes, including heavy metal ions [24,25].

SPR is an optical process in which light satisfying a resonance condition excites a charge-density wave propagating along the interface between a metal and dielectric material by monochromatic and p-polarized light beam [26]. The intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow due to the resonance occurs between the incident beam and surface plasmon wave. This phenomenon is called surface plasmon resonance. The first sensing application of SPR technique was reported by Liedberg et al. [27]. Since then, numerous SPR sensing structures for chemical and biochemical sensing have been receiving continuously growing attention from scientific community [28–30]. Since the past few years, the use of SPR as heavy ion metal sensor had been widely studied [31–40]. However, to the best of our knowledge, SPR is yet applied to sensitive and selective detection of Pb^{2+} in aqueous solutions. Hence in this study, we report a Pb^{2+}-selective SPR optical sensor.

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http://dx.doi.org/10.1016/j.snb.2012.03.070

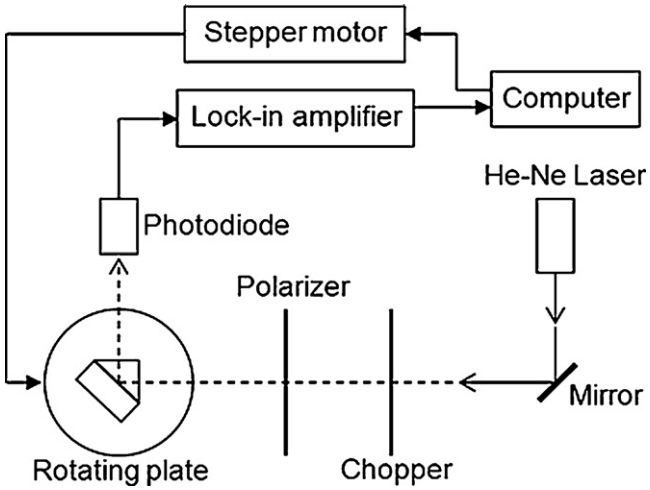

Fig. 1. Experimental setup for angle scan surface plasmon resonance technique.

It is not easy to detect a specific heavy metal ion optically since all heavy metal ions are transparent when they are diluted. Furthermore, the detection work is difficult as they have the similar refractive index [41]. Consequently, we created a surface that can selectively adsorb Pb^{2+} in order to detect the ion in the presence of other metal ion in solution. Chitosan as a chelating agent in absorption of metal ion is well known and has been reported [42–50]. In this work, an attempt has been made to immobilize p-tert-butylcalix[4]arene-tetrakis (BCAT) inside chitosan thin film [51]. The potential of BCAT immobilized chitosan thin film as an active layer for Pb^{2+} sensitive and selective detection in SPR optical sensor is described in this paper.

2. Materials and methods

2.1. Materials and reagents

Medium molecular weight (MMW) chitosan with MW of 190,000–310,000 and degree of deacetylation 75–85% and acetic acid (assay ≥ 99.7%) were purchased from Sigma Aldrich (St. Louis, MO, USA). The crosslinker, glutaraldehyde (25% aqueous solution) was purchased from Alfa Aesar (Ward Hill, MA, USA). The p-tert-butylcalix[4]arene-tetrakis (BCAT) with empirical formula $C_{60}H_{84}N_4O_4S_4$ was obtained from Fluka (Buchs, Switzerland). Atomic Adsorption Spectroscopy standard solution (1000 ppm) of Pb^{2+}, Cu^{2+}, Hg^{2+}, Zn^{2+} and Mn^{2+} ions was purchased from Merck (Darmstadt, Germany).

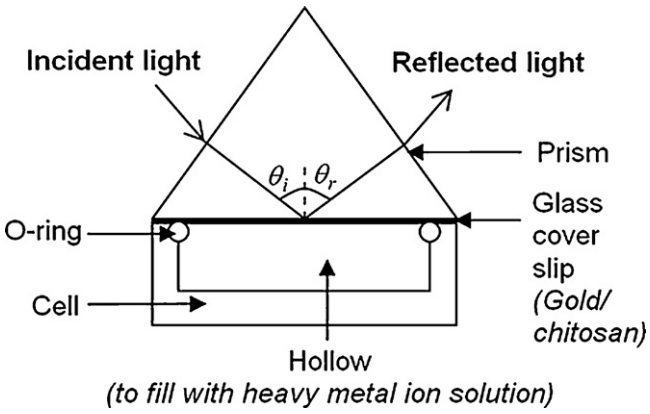

Fig. 2. Structure of the cell for SPR measurement.

2.2. Preparation of chemicals

All chemicals used were of analytical grade and deionized water was used throughout for solution preparation. A stock BCAT solution of 2.0×10^{-3} g/ml or 0.20% (w/v) was prepared by dissolving 50 mg of BCAT in 25 ml deionized water. Chitosan solution was prepared by dissolving 0.40 g of medium molecular weight chitosan in 50 ml of 1% acetic acid, 0.05 g of glutaraldehyde was added to the solution, and then the mixture was stirred thoroughly. Working standard solutions of Pb^{2+} were prepared by appropriate dilution of the 1000 ppm standard solution before used. Multiple metal ion solutions ($Pb^{2+}Cu^{2+}$, $Pb^{2+}Hg^{2+}$, $Zn^{2+}Mn^{2+}$, $Pb^{2+}Cu^{2+}Hg^{2+}Zn^{2+}Mn^{2+}$, $Cu^{2+}Hg^{2+}Zn^{2+}Mn^{2+}$) were prepared by mixing the diluted solution (1 ppm) of required metal ion.

2.3. Procedure

Glass cover slips (24 mm × 24 mm × 0.1 mm, Menzel-Glaser, Germany) were first deposited with a 50 nm gold layer using an SC7640 Sputter Coater. Immobilization of BCAT inside the chitosan thin film is done by mixing 5 ml of 2.0×10^{-3} g/ml BCAT with 45 ml of 1% chitosan solution. The mixture was stirred thoroughly and spin coated at 6000 rpm for 30 s using Spin Coating System, P-6708D to produce a thin layer of BCAT immobilized chitosan thin film (with thickness of 14 nm) on the top of the gold layer [41,52].

2.4. Instrumentation

The SPR measurements were carried out for the in situ analysis of self-assembled layers using a home-built instrument. The schematic diagram of SPR instrument set-up used in this work is shown in Fig. 1. A 5 mW He–Ne laser (λ = 632.8 nm) was p-polarized and directed to a prism (refractive index, n = 1.77861 at 632.8 nm), with a glass cover slip, which coated with gold/BCAT immobilized chitosan thin film, attached onto one side of the prism. A cell was constructed and attached to the gold/BCAT immobilized chitosan surface to hold the heavy metal ion solution, as shown in Fig. 2. The cell had an O-ring in the middle through which the laser light contacted to the solution. The prism and the cell were mounted on a rotating plate to control the angle of the incident light. The reflected beam was detected by a large area photodiode and then processed by the lock-in-amplifier (SR 530). Fig. 3 shows the characteristics of SPR curves for deionized water and heavy metal ion solution at

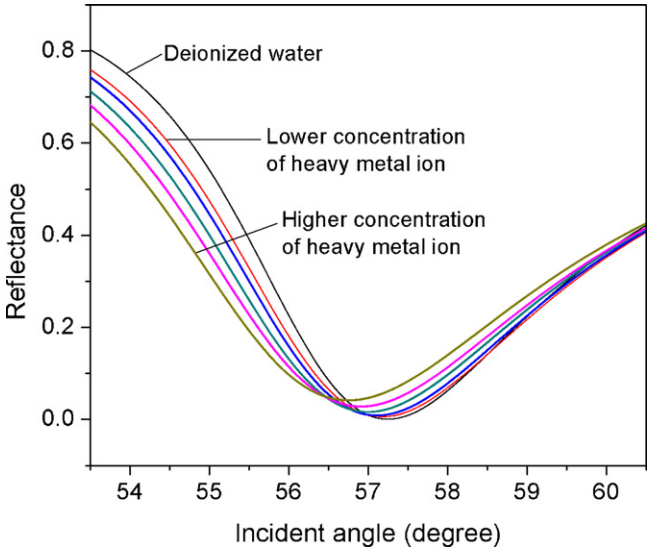

Fig. 3. The characteristic of SPR curve.