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Development of surface plasmon resonance sensor for determining zinc ion using novel active nanolayers as probe

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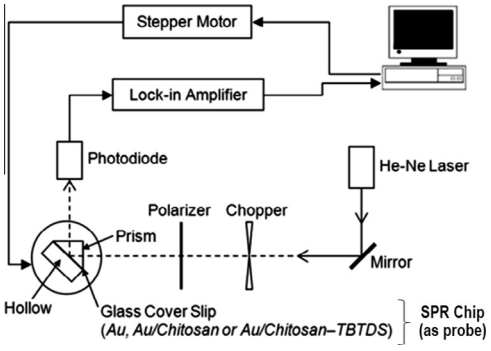
HIGHLIGHTS

- A method for Zn^{2+} detection based on SPR spectroscopy using novel active nanolayer as the probes is proposed.
- The novel active nanolayers are chitosan and chitosan–TBTDS.
- Compare with chitosan nanolayer, the chitosan–TBTDS nanolayer have higher sensitivity for determining Zn^{2+}.
- This method also proved that Zn^{2+} can be selectively detected.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, novel active nanolayers in combination with surface plasmon resonance (SPR) system for zinc ion (Zn^{2+}) detection has been developed. The gold surface used for the SPR system was modified with the novel developed active nanolayers, i.e. chitosan and chitosan–tetrabutyl thiuram disulfide (chitosan–TBTDS). Both chitosan and chitosan–TBTDS active layers were fabricated on the gold surface by spin coating technique. The system was used to monitor SPR signal for Zn^{2+} in aqueous media with and without sensitivity enhancement by TBTDS. For both active nanolayers, the shift of resonance angle is directly proportional to the concentration of Zn^{2+} in aqueous media. The higher shift of resonance angle was obtained for chitosan–TBTDS active nanolayer due to a specific binding of TBTDS with Zn^{2+}. The chitosan–TBTDS active nanolayer enhanced the sensitivity of detection down to 0.1 mg/l and also induced a selective detection towards Zn^{2+}.

Introduction

Transition metal ions such as Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} are essential nutrients to maintain human metabolism. Zn^{2+} is one of the most abundant transition metal ions in the human body that plays important roles in a wide variety of metabolic processes including acts as neural signal modulator, structural cofactor and gene expression regulator [1–4]. Thus, Zn^{2+} is important for normal growth during pregnancy, childhood and adolescence [5]. However, Zn^{2+} cannot be consumed over the daily limit or else it is potential for toxicity. Recommend Dietary Allowance (RDA) of Zn^{2+} is 11 and 8 mg/day, for men and women, respectively [6]. The excessive ingestion of Zn^{2+} may cause severe irritation to the

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gastrointestinal, as well as fever, chest pain, chills, cough, dyspnea, nausea, muscles soreness, fatigue and leukocytosis.

Several conventional methods have been developed for trace metal analysis including Zn^{2+} in aqueous media. The methods with application in routine analysis that normally used include atomic absorption spectroscopy (AAS) [7–10], inductively coupled plasma mass spectrometry (ICPMS) [11–14], X-ray fluorescence spectrometry (XRF) [15–18], instrumental neutron activation analysis (INAA) [19–21] and anodic stripping voltammetry (ASV) [22–26]. Overall, these existing techniques have one or several disadvantages. For instance, AAS is destructive, requires a long measurement period and can only determine one element in one time. ICPMS is bulky and not selective to different charge stats and chemical forms of an element. In addition, AAS and ICPMS are very high cost techniques. On the other hand, the disadvantage of XRF is the characteristic of high self absorption of emitted radiation limiting the analysis to thin films or surface layers, while INAA requires access to a high-flux neutron source to obtain the sensitivity. Although voltammetric methods are simple, inexpensive and portable, they could be subjected to interferences inherent in complex sample matrices. Also, ASV can only measure amalgam-forming metal species. Therefore, complementary method such as optical sensor is being developed to overcome some of these drawbacks. Surface plasmon resonance spectroscopy, one of the optical sensors, is a high potential alternative for detection of metal ions owing to its proven advantages such as cost-effective, portable, fast measurement capability, simple preparation of sample and no necessity of reference solution [27–29].

Surface plasmon resonance (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 [30]. The intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow (the phenomenon of SPR) due to the resonance energy occurs between the incident beam and surface plasmon wave. On the other hand, while the incident light is totally reflected the electromagnetic field component penetrates an evanescent wave into the dielectric medium. The evanescent wave propagates along the interface and decays exponentially with distance normal to the interface. This wave is very sensitive to changes in the refractive index near the metal surface. Such a change may result in a shift of the resonance angle at a constant wavelength [31]. Thus, SPR has emerged as a powerful optical sensor based on the sensing of the change in refractive index of a medium adjacent to the metal surface layer. The first sensing application of SPR technique was reported by Liedberg et al. [32]. Since then, numerous SPR sensing structures for chemical and biochemical sensing have been receiving continuously growing attention from scientific community [33–35]. Since the past few years, the use of SPR as metal ion sensor has been studied [36–42]. However, to the best of our knowledge, SPR is yet applied to sensitive and selective detection of Zn^{2+} in aqueous solutions. Hence in this study, we report a Zn^{2+}-sensitive–selective SPR sensor.

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 [43]. Consequently, we created a surface that can selectively adsorb Zn^{2+} in order to detect the ion in the presence of other metal ion in solution. In this study, chitosan has been chosen as the main matrix for our novel active nanolayers. Chitosan is one of the most available biopolymer in nature where it can be derived from alkaline N-deacetylation of chitin, which is the major component of crustaceans shells. Chitosan is chosen due to the presence of the amine functionality on the chitosan chain, confers both polyelectrolyte and chelate properties, which plays an important role in the adsorption of metal ion [44–51]. In addition, chitosan is a low cost material and can be prepared and obtained easily. In order to enhance the sensitivity and selectivity towards Zn^{2+}, an attempt has been made to dope tetrabutyl thiuram disulfide into the chitosan matrix. Tetrabutyl thiuram disulfide, a zinc ionophore, is envisaged to provide a sensitive and selective determination of Zn^{2+} owing it poses sulfur donor atoms which have stronger affinity towards zinc ion [52]. The potential of chitosan and chitosan–TBTDS active nanolayers as the probes for Zn^{2+} sensitive and selective detection in SPR sensor is described in this paper.

Materials and methods

Reagents and chemicals

Medium molecular weight (MMW) chitosan with MW of 190,000–310,000 and degree of deacetylation 75–85% and acetic acid (assay $\geqslant$ 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 tetrabutyl thiuram disulfide (TBTDS) was obtained from Fluka (Buchs, Switzerland). Atomic Adsorption Spectroscopy standard solution (1000 ppm) of Zn^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+} and Mn^{2+} ions was purchased from Merck (Darmstadt, Germany).

Stock and working standard solutions

All chemicals used were of analytical grade and deionized water was used throughout for solution preparation. A stock TBTDS solution (20% w/v) was prepared by dissolving 100 mg of TBTDS in 50 ml deionized water. Working standard solutions of Zn^{2+} were prepared by appropriate dilution of the 1000 mg/1 standard solution before used. Multiple metal ion solutions ($Zn^{2+}Mn^{2+}$, $Zn^{2+}Pb^{2+}$, $Mn^{2+}Cu^{2+}$, $Zn^{2+}Pb^{2+}Mn^{2+}Hg^{2+}Cu^{2+}$, and $Pb^{2+}Mn^{2+}Hg^{2+}Cu^{2+}$) were prepared by mixing the diluted solution (1 mg/l) of the required metal ion.

Preparation of active nanolayers

Glass cover slips ($24 \times 24 \times 0.1$ mm^3, Menzel–Glaser, Germany) were first deposited with a gold (Au) nanolayer (50 nm) using an SC7640 Sputter Coater. Then, spin coating technique (Specialty Coating System, P-6708D) was used to produce an active nanolayer on the top of the gold layer. Before the spin coating process, the active layer solution was prepared.

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. Immobilization of TBTDS inside the chitosan nanolayer is done by mixing 5 ml of 20% w/v TBTDS with 45 ml of 1% chitosan solution.

Approximately 0.55 ml of the solution (chitosan or chitosan–TBTDS) was placed on the glass cover slip covering the majority of the surface. The glass cover slip was then spun separately at 6000 rpm for 30 s to produce chitosan and chitosan–TBTDS active nanolayers.

SPR system

The SPR measurements were carried out for the in situ analysis of the chitosan-based nanolayars using a custom-built instrument. 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 SPR chip (glass cover slip), which coated with Au, Au/chitosan or Au/chitosan–TBTDS films, attached onto one side of the prism. A cell