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Original research article

Sensitivity enhancement of localized SPR sensor towards Pb(II) ion detection using natural bio-polymer based carrageenan

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ABSTRACT

This work demonstrates the employment of a natural biopolymer-based kappa-carrageenan (κCarr) and chitosan (CS) for Pb(II) ion detection using LSPR sensor. κCarr and CS are utilized as active layers on top of gold nanoparticle (AuNP) in LSPR sensor. The characterization of these materials is carried out using Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), field emission scanning electron microscopy (FESEM) and X-ray diffractions (XRD) analysis. FTIR analysis exhibits that, κCarr has O═S = O, O─H and C–O functional groups, meanwhile CS has O─H, N─H and C–O functional groups. This shows that κCarr possesses more oxygen atom in its structure. AFM measurement further proves this result whereas a high surface roughness is observed for AuNP-κCarr compared to AuNP-CS due to the plenty of oxygen atoms on the surface of AuNP-κCarr, therefore AuNP-κCarr is able to provide more active sites for adsorption of Pb(II) ion. In LSPR sensing, the shift in reflectance for κCarr exhibits a linearity response of $R^2 = 0.9722$ and a sensitivity of 1.3535 nm ppm^{-1}, meanwhile CS exhibits a linearity response of $R^2 = 0.6086$ and a sensitivity of 0.8165 nm ppm^{-1} upon exposure to Pb(II) ion. Based on these results, κCarr shows a better linearity response and a higher sensitivity in comparison to CS when it is exposed to Pb(II) ion, hence proves that κCarr is the best sensing material in this study.

1. Introduction

Localized surface plasmon resonance (LSPR) is a highly sensitive optical technique for chemical and biochemical analysis, based on collective oscillation of the free electrons in metallic nanoparticles driven by electromagnetic wave at the nanometallic surface [1]. LSPR had been used widely for detection of Pb(II) ion using various kind of sensing materials. Recently, several research groups have studied the use of material that contain polar functional groups such as amino and sulphate groups for detection of Pb(II) ion [2–4]. For instance, Lin and Chung [2], used monoclonal antibody immobilized onto gold nanoparticle-modified optical fibre, Alizadeh et al. [3] utilized azacrown ether-functionalized gold nanoparticles and Qiu et al [4] used copolymer nanoparticles of self-assembly gold nanoislands functionalized by poly(m-phenylenediamine-co-aniline-2-sulfonic acid) as sensing materials for Pb(II) ion detection. In other report, Guo et al. [5] utilized glutathione modified $Cu_{2-x}S$ nanocrystals for the entrapment of Pb(II) ion based on

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$Cu_{2-x}S$ nanocrystals aggregation. The limit of detection (LOD) reported previously was 0.27 ppb with monoclonal antibody immobilized onto gold nanoparticle [2], 0.01 ppb with copolymer nanoparticles [4] and 52.50 ppb with glutathione modified $Cu_{2-x}S$ nanocrystals [5]. Although these materials able to sense and adsorb Pb(II) ion with low detection limits, they suffered from a long and complicated synthesis process.

Therefore, LSPR based polysaccharides had been studied by numerous researchers [6,7] recently, as it offers the advantages of low-cost and environmental friendly [7,8]. Chitosan is a type of polysaccharides which consist of β-(1–4)-2-acetamido-D-glucose and β-(1–4)-2-amino-D-glucose units and commonly used in detection of heavy metals. The growing interest to explore the use of chitosan in wastewater treatment for the removal of heavy metal particularly is due to its natural chelating properties whereby it can bind and remove the heavy metal ions from wastewater [7]. CS has the ability to adsorb Pb(II) ion due to the presence of amino ($-NH_2$) and hydroxyl ($-OH$) groups in its structure as reported by many researchers [6,7]. Recently, Lokman et al [7] used gold-chitosan-graphene oxide (Au/CS/GO) nanostructured thin films to detect Pb(II) ion using SPR sensor with high sensitivity of 1.11200 ppm^{-1} compared to 0.77600 ppm^{-1} for gold-chitosan (Au/CS) film. Other optical techniques for detection of heavy metals have also been reported in the literature [9–13].

Another type of polysaccharides that had potential to be used is carrageenan. Based on our literature studies, there are no LSPR based on carrageenan had been developed. Carrageenan is a type of polysaccharides which extracted from red seaweed (marine red algae) of the Rhodophycea family [8]. It can be divided into three primary types; kappa-carrageenan (κCarr), iota-carrageenan (ιCarr) and lambda-carrageenan (λCarr) based on their degree of sulfation [14]. Generally, all types of carrageenan contain sulphate and hydroxyl groups in its structure [15]. Transparent, flexible, high ionic conductivity, ability to conduct electricity and environmental friendly are some of the properties of κCarr [8]. Khotimchenko et al [14] studied the chemical structure and physicochemical properties of different types of carrageenan for the creation of new drugs that able to eliminate Pb(II) and Y(III) ions from human body. It was reported this material is highly potential to be applied for binding and removing the metal ions from aqueous solution, however the binding capacity of the carrageenan towards Pb(II) and Y(III) ions were affected by the chemical structure and physicochemical properties of these carrageenan.

The previous work of Bang and Pazirandeh [16] reported the use of κCarr for removal of heavy metal displayed a better result compared to CS and alginate with approximately 48%, 20% and 8% respectively because of the good ionic strength characteristic possessed by κCarr [16]. This is due to the presence of polar functional groups in κCarr structure [16]. Based on this work [16], it showed that κCarr possessed high tendency to adsorb Pb(II) ion and is highly potential to be applied in the sensing field. The sensitivity of detection could be enhanced by the incorporation of gold nanoparticle (AuNP) with this material [7]. Herein, we report the application of gold nanoparticle- κCarrageenan (AuNP-κCarr) as a sensing material for Pb(II) ion detection. Firstly, the sensing materials were prepared by growing the AuNP on top of ITO/glass substrate and coating it with κCarr and CS which acted as active layers for Pb(II) ion sensing. The sensing materials were characterized using FTIR, AFM, FESEM and XRD to study the properties of the materials which may influence the performance of sensors. Thereafter, the LSPR analysis were carried out for detection of Pb(II) using AuNP-κCarr and gold nanoparticle-Chitosan (AuNP-CS) as the sensing materials and the sensor performances were compared. To the best of our knowledge the use of AuNP-κCarr material for detection of Pb(II) ion by LSPR has not yet been explored.

2. Materials and methods

2.1. Materials and reagents

κ-Carrageenan was purchased from Fluka (Switzerland). Chitosan was commercially obtained from Chito-Chem (Malaysia). Cetyltrimethylammonium bromide (CTAB), poly-*l*-lysine (PLL), gold chloride tetrahydrate ($HAuCl_4$) were purchased from Aldrich (USA). L-ascorbic acid and trisodium citrate were purchased from Wako Pure Chemical Industries (Japan), sodium borohydride ($NaBH_4$) was purchased from Merck (Germany). Indium tin oxide (ITO) was commercially obtained from Latech Scientific (Singapore). Sodium hydroxide (NaOH) was purchased from R & M Chemicals (Essex, UK). Acetic acid was purchased from Systerm Chemicals (Malaysia). All chemicals were of analytical grade.

2.2. Methodology

2.2.1. Preparation of sensing materials

i. Characterization of κCarr and CS powders

ATR-FTIR analysis was carried out using Perkin-Elmer Spectrum 2000 (USA) in the range of 4000-400 cm^{-1} with scanning resolution of 4 cm^{-1}. This analysis was conducted to observe the functional groups present in both κCarr and CS structures which affect the performance of the sensor. X-ray Diffraction (XRD) analysis was performed using a Siemens D5000 diffractometer (USA) with CuKα radiation ($\lambda = 1.5406$ Å) and an angular scanning range (2θ) from 20° to 60° to study the physical and material phase of κCarr and CS powders.

ii. Preparation of κCarr and CS solutions

12.5 g of κCarr and CS each was dissolved in 25 mL of 1% acetic acid separately [6,7]. Afterward, the solution was stirred for 24 h to form a homogeneous solution.

iii. Assembly of AuNP on ITO/glass substrate

Gold nanoparticles were synthesized via seed-mediated technique [17]. The indium tin oxide/glass (ITO/glass) substrates with a dimension of 1 cm x 1 cm were cleaned using ultrasonic and immersed in PLL for 30 min. The seed solution was prepared by