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Preparation of Ion Imprinted SPR Sensor for Real-Time Detection of Silver(I) Ion from Aqueous Solution

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The aim of the submitted study is to develop molecular imprinting based surface plasmon resonance (SPR) sensor for real-time silver ion detection. For this purpose polymeric nanofilm layer on the gold SPR chip surface was prepared via UV polymerization of acrylic acid at 395 nm for 30 minutes. N-methacryloyl-L cysteine used as the functional monomer to recognize the silver(I) ions from the aqueous solutions and methylene bisacrylamide used as the crosslinker for obtaining structural rigidity of the formed cavities. Silver(I) solutions with different concentrations were applied to SPR system to investigate the efficiency of the imprinted SPR sensor in real time. For the control experiments, non-imprinted SPR sensor was also prepared as described above without addition of template "silver(I) ions". Prepared SPR sensors were characterized with atomic force microscopy (AFM). In order to show the selectivity of the silver(I) imprinted SPR sensor, competitive adsorption of Cu(II), Pb(II), Ni(II) ions was investigated.

Keywords: Molecular imprinting, Surface Plasmon Resonance, Ion sensor, Silver(I).

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1. INTRODUCTION

Although metals play important roles in biological processes and some of them are classified as essential elements, hazardous properties will occur when metal ions level exceeds a certain threshold concentration. Accumulation of heavy metal ions in the body leaves permanent damages and causes many diseases. For this reason, monitoring and quantification of heavy metal ions become important.

Silver ions are used on the surfaces of water filters due to the anti-microbial properties. In addition, silver nanoparticles are also widely used with the development in nanotechnology. Due to large scale use of silver in industrial applications, these ions contaminate water sources via leakage of the industrial wastes. Chronic intake of silver products to body can result in an accumulation of silver or silver sulfide particles in the skin. These particles in the skin become darker with exposure to sunlight and the skin gets a color of blue or gray which is called as argyria.

SPR is an optical technique that uses an electron charge density wave phenomenon to measure changes in refractive index very close to a sensor surface. Because of unique properties of SPR sensors, i.e., real-time measurement, high specificity and sensitivity, no need to labeling, the applications of them have been getting more popular for investigation[1].

Molecular imprinting technique, based on molecular recognition, provides the polymerization of synthetic materials, which have specific binding sites and geometric shapes in their high cross-linked structure for the target analyte[2]. Molecular imprinting has been used successfully for imprinting of small molecules, metal-ions and proteins.

2. EXPERIMENTAL

2.1 Materials

L-Cysteine methylester and methacryloyl chloride was also supplied by Sigma (St Louis, USA) and used as received. N-N′-Methylenebisacrylamide (N,N′-MBAAm), was obtained from Fluka A.G. (Buchs, Switzerland). All other chemicals were of analytical grade purity and were purchased from Merck AG (Darmstadt, Germany). All water used in the experiments was purified by a Barnstead (Dubuque, IA) ROpure LP® reverse osmosis unit having a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NANOpure® organic/colloid removal and ion exchange packed-bed system.

2.2 Surface Plasmon Resonance (SPR) Apparatus

The recognition of the prepared polymers toward the analyte silver(I) was performed by using chips which made of a high refractive index glass prism coated with a thin gold film and the change in the incident angle ($\Delta\theta$) responding to the addition of substrates was recorded on the SPR apparatus (Genoptics, France)[3].

2.3 Preparation of Functional and Metal-Chelate Monomers

Briefly, the following experimental procedure was applied for the synthesis of N-methacryloly-(l)-cysteinemethylester (MAC) monomer: 5.0 g of cysteine and 0.2 g of $NaNO_2$ were dissolved in 30 ml of K_2CO_3 aqueous solution (5%, v/v). This solution was cooled to 0 °C. 4.0 ml of methacryloyl chloride was poured slowly into this solution under nitrogen atmosphere and then, this solution was stirred magnetically at room

temperature for 2 h. At the end of this period, the pH of this solution was adjusted to 7.0 and was extracted with ethylacetate. The aqueous phase was evaporated in a rotary evaporator. The residue (i.e., MAC) was crystallized in ethanol and ethylacetate[4].

The complex monomer, MAC-Ag^+, was prepared by slow addition of solid N-methacryloyl-(l)-cysteine methylester (MAC) into 1 ml solution of ethanol–water mixture (50/50, v/v) in a vessel followed by dissolution of silver (I) nitrate at room temperature by constant stirring (250 rpm) for 2 h.

2.4 Preparation of Silver(I) imprinted SPR Sensor

In order to clean the sensor surface, the sensor was immersed in 20 mL of acidic piranha solution (3:1 H_2SO_4:H_2O_2, v/v) for 30 s. Then, it was washed with pure ethyl alcohol and dried in vacuum oven (200 mmHg, 37◦C) for 3 h. Later on, the sensor was immersed in ethanol/water (4:1, v/v) solution containing 3-mercaptopropene for 12 h. For the polymerization, the reaction mixture containing the metal-chelate (MAC-Ag^+) monomer, N,N′-MBAAm crosslinking monomer, acrylic acid and initiator was prepared. Then, the reaction mixture was degassed and dropped on the gold surface of SPR sensors. Pure nitrogen gas was purged in to the cell for 5 min to evacuate the air completely since the presence of oxygen would prohibit polymerization. Polymerization was carried out at room temperature applying UV light irradiation under nitrogen atmosphere (polymeric nanofilm layer on the gold SPR sensor surface) for 30 min. The non-imprinted polymer-coated SPR sensor, as a control, was also prepared in a similar manner in the absence of template ions by the same polymerization procedure.

2.5 Evaluation of SPR-MIP sensor response

Changes in the refractive indexes on silver (I) imprinted gold surface are recorded by a CCD camera as gray-level contrasts using surface plasmon resonance apparatus model SPR (Genoptics) which was designed and implemented using the Kretschmann configuration. Measurements were carried out in a Teflon cell connected to a peristaltic pump in phosphate buffer solution at room temperature.

3. RESULTS AND DISCUSSION

In this study, we have attempted combining of molecular imprinting technology and SPR sensor approaches and producing SPR sensor for real-time detection of silver(I).

Silver(I) imprinted SPR sensor has a high sensitivity with a wide range of silver concentrations (0.05 - 50 ppm) in aqueous solutions. The increasing concentration of silver in solution caused the increasing response of the sensor, because resonance frequency shift (ΔR) depends on the concentration of silver(I). The results of competitive adsorption of Ag(I) with Ni(II), Cu(II), Pb(II) indicate that Ag(I) imprinted SPR sensor have higher adsorption capabilities for Ag(I) than for other analytes. Non-imprinted SPR sensor did not give any significant response to solution containing Ag(I), Pb(II), Ni(II) and Cu(II) ions. In order to show the reproducibility of silver(I) imprinted SPR sensor response, three equilibration-adsorption-regeneration cycles were repeated by aqueous silver(I) solution which has the same concentration. After the completion equilibration-adsorption-regeneration cycles, reusa-bility of the SPR sensor was determined.

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