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ORIGINAL PAPER

Development of a metal-island-coated swelling/shrinking copolymer sensor for measurement of divalent metal ions

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Abstract A copolymer of *N*-vinylimidazole and *N*-vinyl-2-pyrrolidone, photo-crosslinked with sulfonated diazidostilbenes, showed swelling/shrinking behaviour due to interaction with divalent metal ions such as Mn^{2+}, Zn^{2+}, Ni^{2+}, and Co^{2+}. This effect was used to set up a resonance enhanced absorption chip; a solution of the copolymer in methanol, stabilized with the radical scavenger 2,6-di-*t*-butyl-4-methylphenol, was spin-coated onto a silanized aluminum chip and then sputtered with gold nanoparticles. The change in layer thickness caused by the interaction of ions with the copolymer interlayer resulted in a shift of the maxima of the reflection spectrum to lower wavelengths and thus also a visible colour change. This spectral shift was logarithmically related to the concentration of metal ions. Mn^{2+} turned out to react more rapidly and was detected with 100-fold greater sensitivity than the other investigated ions.

Keywords Sensor · Metal island · Copolymer *N*-vinylimidazole/*N*-vinyl-2-pyrrolidone · Swelling/shrinking · Divalent metal ions

Introduction

Metal nanoclusters in the size range from 1 nm to approximately 1 μm possess completely different physical and optical behaviour than macroscopic structures in solid metals. When excited by electromagnetic radiation they show special absorptive properties due to the restricted electron mobility in the clusters, which can form the basis for promising applications. If positioned near a mirror, the optical properties of these nanocluster metal-island films [1, 2] enable the transduction of molecular binding events into visually detectable signals caused by so-called anomalous absorption. For a certain separation of the absorbing layer from the mirror, the electromagnetic field reflected by the mirror has the same phase at the position of the absorbing layer as the incident fields, which results in a feedback mechanism that strongly enhances the effective absorption coefficient of the absorbing layer. As, for a given interlayer distance, this optimum phase relation only occurs for a defined wavelength, the system is characterized by a narrow spectral reflection minimum, whose spectral position shifts sensitively with the interlayer thickness and whose intensity strongly depends on the surface coverage with clusters.

Aussenegg et al. [3] applied a metal-island-coated swelling polymer over mirror system (MICSPOMS), which consisted of a highly reflecting mirror as support for the chip, a nanometric interlayer with defined analyte-sensing properties and the metal-cluster layer to transduce the signal received from the copolymer interlayer to measure the ionic strength. An optical sensor with a metal-island copolymer sensitive to changes in the concentration of anions due to swelling or shrinking was described by Schalkhammer et al. [4]. Metal ions such as copper and zinc cause swelling in a copolymer consisting of

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2-hydroxyethyl methacrylate/ethylene glycol methacrylate and azobisisobutyronitrile suspended in a polyurethane hydrogel membrane. This leads to a decrease of membrane turbidity, which can be used for sensing [5]. Another approach to detect metal ions is also based on a swelling copolymer, in this case containing ligands for complexation of the ions. The copolymer is additionally labelled with two fluorescent molecules. After binding of copper ions, the change of particle size causes a change in the ratio of the fluorescence intensities of the two fluorophores [6]. A novel pH sensor is based on the swelling of a polyvinylalcohol/polyacrylic acid hydrogel located on a piezoresistive pressure sensor chip [7, 8]. Recently, Odeh et al. [9] synthesized a sensing element consisting of dithiocarbamate-polymer microspheres dispersed in a hydrogel. Metal ions, especially Hg^{2+}, formed complexes with the dithiocarbamate functionality, which resulted in a decrease of optical transmission through the sensing membrane.

The objective of this work is to synthesize a stable transparent adhesive copolymer sputtered with gold nanoparticles for use as a layer sensitive to metal ions on an aluminum plate. The colour change or spectra shift caused by swelling/shrinking of the copolymer is used to quantitate the metal ions.

Results and discussion

Synthesis of the copolymer

The main objective was to synthesize a stable copolymer with controlled swelling/shrinking properties on interaction with divalent metal ions. For this purpose different amounts of *N*-vinyl-2-pyrrolidone and *N*-vinylimidazole and various amounts of radical starter were tested. The greatest stability of the copolymer in water and metal ion solutions during the measuring period was found experimentally to be when *N*-vinyl-2-pyrrolidone (A) and *N*-vinylimidazole (B) solutions were mixed in a volume ratio of $V_A/V_B = 1{:}9$ for synthesis. The quality of the sensor layer was influenced by the amount of the starter compound α,α'-azoisobutyronitrile. At low mass concentrations (25 mg/15 cm^3) an unstable copolymer, which was easily detachable from the aluminum foil by double-distilled water, was formed. Addition of 50 mg/15 cm^3 of α,α'-azoisobutyronitrile resulted in a more stable layer, but the interaction with metal ions caused only small spectral shifts of the second maximum. Best results were achieved when using 75 mg/15 cm^3 of the starter compound, whereas applying 100 mg/15 cm^3 or more resulted in diminished sensitivity of the layer to bivalent metal ions. After dissolution of the copolymer in methanol and addition of the radical scavenger 2,6-di-*t*-butyl-4-methylphenol, the compound was stabilized so that it could be stored for weeks without losing its swelling/shrinking properties. Omission of the inhibitor during sensor chip preparation resulted in a sensitive layer for which the position of the maxima in the absorption spectrum changed each day; additionally, the stability of the sensor chips was reduced within 2 weeks, and the layer could be detached by mere immersion of the chip in a metal ion solution.

Synthesis of the copolymer under these definite experimental conditions results in a transparent compound, and addition of the radical scavenger enhances the shelf-life of its solutions in methanol to over 3 months, when stored at −18 °C.

Preparation of sensor chips

The aminosilanized sensor chip was positioned in the centre of a spinning plate. Rotation at 1,800–3,000 rpm resulted in thin and reproducible layers, whereas for low rotation speeds (<1,000 rpm) inhomogeneous sensor layers were formed. Attempts to coat more chips at the same time resulted in inhomogeneous chips, especially in the outer zone of the plate. Cross-linking of the copolymer with 4,4′-diazidostilbenedisulfonic acid disodium salt tetrahydrate during 30 min by means of ultraviolet (UV) lamp radiation (254 nm, 40 W) as well as spinning for 100 s resulted in reproducible sensor chips. These chips were then sputtered with gold nanoparticles and remained stable for at least 4 weeks when stored. The colour of faultless chips was blue; stained chips were discarded.

Spectroscopic measurement

The sensor chips were conditioned in double-distilled water before exposure to bivalent metal ion solutions, which changed the colour of the surface from blue to red. This colour modification could be tracked by spectroscopic measurement. For this purpose the wet sensor chip was inserted with the sensitive layer downward into a glass cuvette with a filmy glass bottom. This ensured that the sensor chip was placed at a definite position during the measurement and that repeated spectra measurements were reproducible. The spectra showed two significant maxima (Fig. 1).

Exposure of the chips to different concentrations of metal ions resulted in colour change from red to green [$c(Mn^{2+}) = 10^{-6}$ M] to blue [$c(Mn^{2+}) = 10^{-3}$ M] and red [$c(Mn^{2+}) = 10^{-2}$ M]. The shift of the second maximum at higher wavelengths was measured as a function of the concentration of manganese ions (Figs. 2, 3), showing a logarithmic relationship (Fig. 4) between the shift of the maximum (response) and the concentration. Zinc, cobalt, and nickel ions showed similar behaviour.

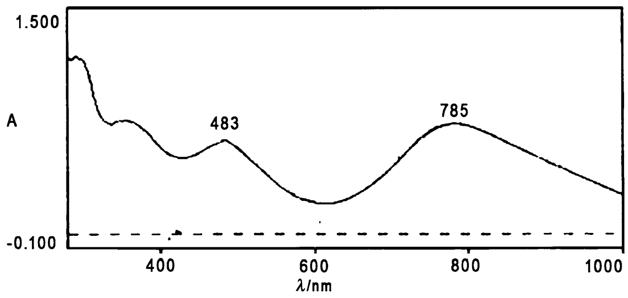

Fig. 1 Spectrum of a sensor chip in distilled water (colour: red)

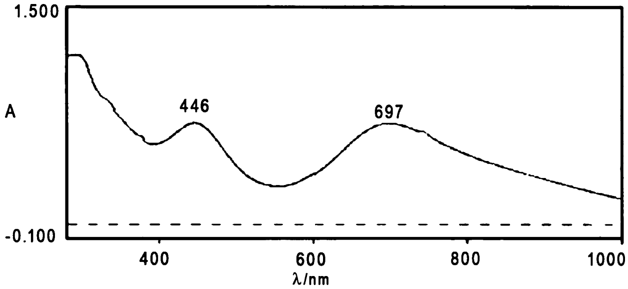

Fig. 2 Spectrum of a sensor chip in 10^{-6} M manganese sulfate (colour: green)

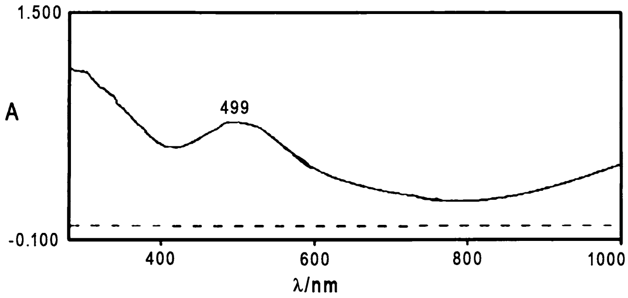

Fig. 3 Spectrum of a sensor chip in 10^{-2} M manganese sulfate (colour: reddish)

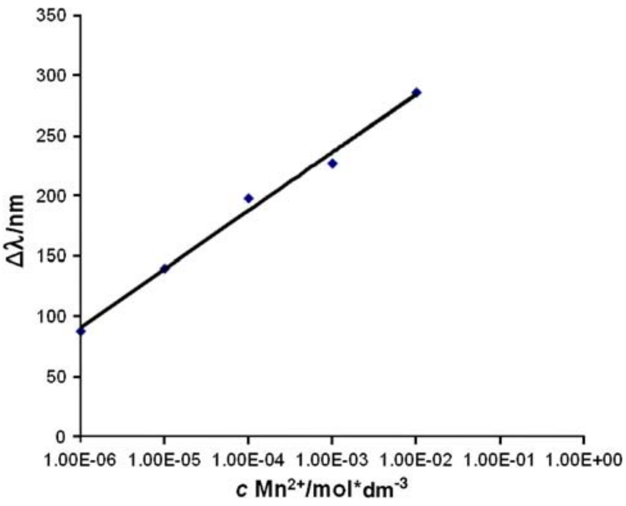

Fig. 4 Calibration curve for manganese ions

Table 1 Relation between the response (shift of the maximum, $\Delta\lambda$) and concentration of metal ions

Metal ion	Δλ (nm)					
	c					
	10^{-6} M	10^{-5} M	10^{-4} M	10^{-3} M	10^{-2} M	10^{-1} M
Nickel	–	–	18	25	83	117
Cobalt	–	–	26	88	126	–
Zinc			163	227	249	–
Manganese	88	140	198	227	286	–

Reactivity and sensitivity

The reactivity and sensitivity of the sensor chips was quite different for different ions. Low manganese concentrations (e.g. 10^{-6} M) in contact with the sensor chip reacted within 1 min, whereas zinc, cobalt, and nickel ions needed between 5 and 10 min, respectively, even at higher concentrations (e.g. 10^{-4} M) to cause a change in the layer thickness.

The sensitivity of the chip also differed for certain metal ions (Table 1). The detection limit for manganese ions was 10^{-6} M, whereas for nickel, cobalt, and zinc ions, changes started at concentrations exceeding 10^{-5} M.

N-Vinylpyrrolidone as well as *N*-vinylimidazole form hydrogels and copolymers were used in metal ion adsorption studies. These polymers showed swelling behaviour and retention of bivalent metal ions [10–12]. Complexes of metal ions were formed with *N*-vinylpyrrolidone and *N*-vinylimidazole polymers, as well as with copolymers of these compounds. Four imidazole units can bind to one metal ion [13] and can cause conformational changes in the poly(*N*-vinylimidazole) polymers [14]; in the polyvinylpyrrolidone segments, interactions take place between metal ions and the carbonyl groups [15]. The sorption kinetics and the sorption capacity depend on pH, copolymer composition, the degree of cross-linking of the copolymers and the kind of metal ions.

The volume ratio *V*(*N*-vinyl-2-pyrrolidone)/*V*(*N*-vinylimidazole) of 1:9 that was found to be optimal for synthesis of the transparent interlayer of the sensor chip was also found to be advantageous for preparation of ion exchangers. Manganese and zinc ions form complexes with the *N*-vinylpyrrolidone/*N*-vinylimidazole copolymers of higher strength than do cobalt and nickel ions. This explains the smaller shifts (Table 1) of the spectral maximum (response, $\Delta\lambda$) for metal ions with lower complexation constants.

Conclusions

The type of sensor described herein relies heavily on the procedure for synthesis of the copolymer. Accurate ratios between the reaction partners and strict experimental conditions are necessary to produce a copolymer of the desired quality. Marginal deviations of synthesis time, solvent and purification conditions of the copolymer resulted in copolymer that was insensitive to the investigated metal ions. However, modification of the experimental parameters might provide sensitivity to other metal ions. Fabrication of the described sensor chips in great numbers is very simple, thereby enabling cheap and reliable production of sensors for metal ions.

Experimental

Substances, reagents, and solvents

N-Vinylimidazole, *N*-vinyl-2-pyrrolidone (99.5%) and 2,6-di-*t*-butyl-4-methylphenol were purchased from Polysciences, Inc. (Warrington, PA, USA). (3-Aminopropyl)diethoxymethylsilane ($\geq$97%), 4,4′-diazidostilbene-2,2′-disulfonic acid disodium salt tetrahydrate ($\geq$99%), α,α'-azoisobutyronitrile (>98%), diethylether, and petroleum ether (b.p. 40–60 °C) were from Fluka (Buchs, Switzerland). Methanol Lichrosolv R was purchased from Merck (Darmstadt, Germany). Cobalt sulfate, manganese sulfate, nickel sulfate, and zinc sulfate were from Merck (Darmstadt, Germany). All chemicals were of analytical grade and used without further purification. Stock solution I: 1 g purified copolymer dissolved in 8 cm^3 methanol. Stock solution II: 500 mm^3 stock solution I, 1,000 mm^3 methanol, 100 mm^3 3% 4,4′-diazidostilbene-2,2′-disulfonic acid disodium salt tetrahydrate. Metal ion stock solutions of each compound (0.1 M) in double-distilled water were prepared and diluted to the appropriate concentrations.

Apparatus

A Hitachi (Tokyo, Japan) U-2000 spectrophotometer adapted with ZEUS NT software developed by Th. Schalkhammer (Department of Biochemistry, University of Vienna and MFPL) and a 5° specular reflectance attachment and self-made cuvette (diameter 15 mm, height 20 mm), adapted with a filmy glass window at the bottom (manufactured by W. Balba, Institute of Organic Chemistry, University of Vienna), were used. Spinning apparatus was constructed and produced by H. Hörschläger, Department of Analytical Chemistry and Food Chemistry, University of Vienna. The sputter coater was a model 108, series 258 (Agar Scientific Ltd., Stansted, Essex, UK).

The UV-A high-power instrument was a Fluorotest Forte, Atlas (230 V, 40 W, 254 nm; UV-Consulting Peschl, Mainz, Germany). The UV exposure unit (400 W, 254 nm) was from Mega Electronic GmbH (Frickenhausen, Germany).

Synthesis of the copolymer

A solution of 0.5 cm^3 *N*-vinyl-2-pyrrolidone, 4.5 cm^3 *N*-vinylimidazole and 15 cm^3 methanol was purged with nitrogen for 1 h, then heated to 72 °C. After 30 min, 75 mg α,α'-azoisobutyronitrile was added to start the radical reaction, and the reaction mixture was held for a further 6 h at 72 °C. Afterwards, the copolymer was rapidly cooled to -18 °C in a refrigerator and stored there overnight. Next morning, the copolymer was dissolved in 20 cm^3 methanol at room temperature, and then 37.5 mg 2,6-di-*t*-butyl-4-methylphenol was added to stop the radical reaction.

Purification of the copolymer

The highly viscous methanolic solution (1 cm^3) was pipetted onto a cover glass and treated several times with diethylether until the copolymer agglomerated. The purified copolymer (1 g) was dissolved in 8 cm^3 methanol (stock solution I) and the solution was stored at 4 °C.

Preparation of the sensor supports

Silanization

Aluminum chips (diameter 12 mm, thickness 0.5 mm) and 6 cm^3 (3-aminopropyl)diethoxymethylsilane were placed in a glass vessel and kept overnight in a vacuum chamber (exsiccator), with vacuum briefly applied. Then the aluminum chips were heated at 105 °C for 1 h in a cabinet dryer.

Spin-coating and cross-linking

The aluminum chips were fixed in the centre of the rotating wheel of a spinning apparatus and washed with 50 mm^3 methanol at 2,500 rpm for 40 s. Afterwards 50 mm^3 stock solution II was spread over the chip and spin-coated at 2,500 rpm for 1 min. Cross-linking of the spin-coated film was done by irradiation with UV light (254 nm for 100 s).

Sputter-coating

A gold foil was inserted into the target holder and the chip was placed on the table inside the vacuum chamber of an Agar sputter coater. The sputtering process itself was carried out using argon plasma. The chamber was evacuated to less then 0.03 mbar and, after washing it intensively with argon at 1 mbar, the pressure was adjusted to 0.1 mbar. Then an electric field of 5 kV was applied.

Within 10 s at a sputter current of 40 mA, gold particles were deposited on the surface of the chip.

Reflection measurement

The response of the copolymer-coated sensor was measured between 280 and 1,000 nm using a Hitachi U-2000 spectrophotometer adapted with a reflection unit. Each sensor chip was conditioned in distilled water transferred into a self-constructed cuvette, and then the spectrum of each chip was measured. Afterwards each sensor chip was placed for about 5 min into an aqueous metal ion solution ($MnSO_4$, $ZnSO_4$, $NiSO_4$, and $CoSO_4$), starting with the lowest concentration (10^{-6} to 10^{-1} M). The spectrum of each chip was recorded, and the shift of the maximum at higher wavelengths was measured as a function of concentration.

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