Surface plasmon resonance analysis of aqueous mercuric ions

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Abstract

Mercuric ions, Hg[II], can be detected and quantitated by measuring the surface plasmon resonance (SPR) signal when a gold film treated with 1,6-hexanedithiol (HDT), which produced a self-assembled monolayer, is exposed to mercury ions in aqueous solution. Changes in the SPR signal allowed not only quantification of the concentration of Hg[II] in solution from 1.0 nM to 1.0 mM but also selective detection of Hg[II] ions when present in mixtures containing Pb[II], Ni[II], Zn[II], and Cu[II] ions.
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1. Introduction

Elemental mercury, inorganic mercury, and methylmercury are the three most important forms of mercury in natural aquatic environments. Because of its extreme toxicity, methylmercury is the most important contaminant. Elemental mercury has a high vapor pressure, a low solubility, does not combine with inorganic or organic ligands, and is not available for methylation. Most mercury is released into the environment as inorganic mercury, which is primarily bound to particulates and organic substances. The mercurous ion, Hg[I], combines primarily with inorganic compounds and cannot be methylated. In contrast, the mercuric ion, Hg[II], combines with both inorganic and organic ligands and can be methylated. Consequently, concentration measurements of mercuric ion in aquatic streams are of great importance in assessing environmental damage and the possible success of remediation efforts.

Several methods exist for determining Hg[II] concentration. They range from polarography to atomic absorption (AA) to inductively coupled plasma (ICP) spectroscopy. In spite of their exact and fast measurement capabilities, recent analytical interest has focused on developing optical sensors. They have the advantages of size, cost-effectiveness, simplicity, no necessity of reference solution, and fieldwork applicability [1–3]. Optical sensors developed to date, how-

ever, require the use of tagging agents or carriers having selective affinity to the target metal ion of interest. In contrast, surface plasmon resonance (SPR) spectroscopy is known as an optical sensor that does not need tagging agents [4].

When *p*-polarized electromagnetic radiation propagates from an optically dense medium into a sparse medium, total internal reflection occurs for incident angles greater than the critical angle, and an evanescent wave is generated in the sparse medium. When this evanescent wave couples with electrons in the sparse medium, the intensity of the reflected light is reduced. This phenomenon is called surface plasmon resonance. Typically, the SPR technique involves the optical excitation of surface plasmon polariton waves on a gold or silver film employing the Kretschmann configuration. Reflectivity, R, is measured as a function of the incident angle, θ, of the probe light beam [5–7]. At a fixed optical wavelength, the $(R - \theta)$ plot usually exhibits an approximately Lorentzian profile, with a reflectivity minimum at the SPR angle, called θ_{SPR}. The presence of an adsorbed sample alters the width, position, and height of the $(R - \theta)$ plot. It also affects the fractional reflectivity change at θ_{SPR}. The species of interest is detected by monitoring these changes. The SPR technique is currently in widespread use in a variety of chemical and biological sensors [8–11]. It is also used to study the conformational changes of molecules or the detection of the heavy metal ion Pb^{2+} [12,13]. To the best of our knowledge, however, SPR has not been applied to the selective detection of heavy metal ions, especially mercuric ion in aqueous solutions. Here, we report a mercury-selective SPR sensor.

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It is difficult to detect optically a specific heavy metal ion because metal ions have similar refractive indices (RIs) and they are transparent when they were diluted. To detect Hg[II] in the presence of other metal ions in solution, we created a surface that selectively adsorbs the Hg[II] ion. We accomplished this task by treating an Au surface with 1,6-hexanedithiol (HDT), which causes a self-assembled monolayer to form. With the help of a split-field photodiode detector whose sensitivity was established in previous investigations of ionization and reprotonation of the mercaptopropionic acid monolayer [14], we measured SPR signals from adsorbed Hg[II]. We found that Hg[II] could be detected selectively in an aqueous solution containing Pb[II], Ni[II], Zn[II], and Cu[II] ions, heavy metal ions that often interfere with other measurement techniques.

2. Experimental

2.1. Materials

1,6-Hexanedithiol (HDT, Aldrich) was used as an adsorption-inducing chemical. Mercury chloride ($HgCl_2$, Sigma), lead chloride ($PbCl_2$, Aldrich), nickel chloride ($NiCl_2$, Aldrich), zinc chloride ($ZnCl_2$, Aldrich), and copper chloride ($CuCl_2$, Aldrich) were used to prepare solutions of metal ions. Sulfuric acid (H_2SO_4, Fisher Scientific) and hydrogen peroxide (H_2O_2, Fisher Scientific) were used to clean the microscope slides on which titanium and gold films were evaporated. Hydrogen chloride (HCl, Fisher Scientific) and sodium hydroxide (NaOH, Mallinckrodt Chemicals) were used to control the pH of the metal solutions. H_2O was purified to more than $18 \, M\Omega$ using a Milli-Q water system (Millipore).

2.2. Preparation of gold substrates

Microscope slides (3 in. × 1 in. SF10, Schott glass technology) were immersed in a piranha solution (containing sulfuric acid and hydrogen peroxide in a 70:30 vol.% ratio) for 2 min. The slides were rinsed with water several times, and thoroughly dried with nitrogen. This treatment caused the surfaces of the glasses to become hydrophilic. Au films were deposited on the clean SF10 microscope slides in a homemade vacuum chamber using Ti binder layers. A quartz crystal microbalance (QCM) monitored the weight of the Ti and Au films, which were measured to be 2 and 48 nm, respectively, in thickness.

2.3. SPR system

The time-resolved SPR measurements were carried out for the in situ analysis of self-assembled layers using a home-built instrument. Fig. 1 presents a schematic diagram of SPR instrument used in this work. A cleaned gold substrate was attached to a SF10 prism (1.5 cm × 1.5 cm right
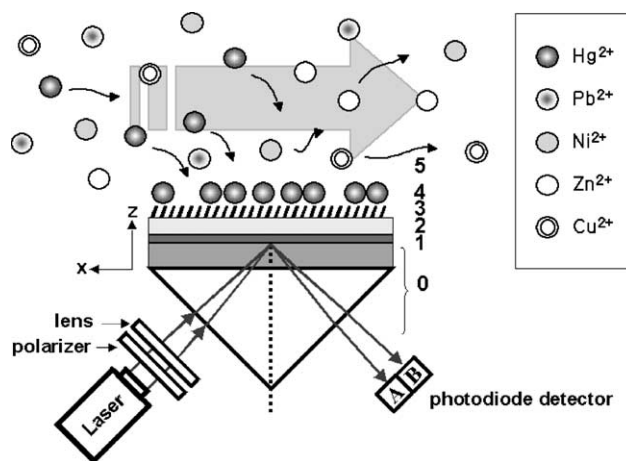

Fig. 1. Schematic of mercury-selective optical detection system using surface plasmon resonance. The p-polarized light was focused on the Au surface, and the reflected light was detected by a split-field photodiode detector. An Au film was prepared on a piranha-treated SF10 microscope slide after evaporating sequentially 2 nm Ti layer: (0) a SF10 glass slide contacting with SF10 prism by an index matching fluid; (1) a binder layer of Ti; (2) Au film; (3) 1,6-hexanedithiol layer; (4) a heavy metal ion layer (Hg[II] in this case); (5) solvent (ethanol or water containing metal ions). The multilayer geometry is described by Cartesian coordinates where the x-axis is along the intersection of the plane of optical incidence and reflection, the (0–1) interface, and the z-axis points toward the subsequent interfaces.

angle prism, CVI) with index matching oil ($n = 1.730 \pm 0.0005$, R.P. Cargille Laboratories Inc.). A Teflon cell was attached to the gold substrate to hold the solution. The 658 nm output of a 30 mW diode laser (LDCU5/4953, Power Technologies) was p-polarized, and focused by a lens through the prism onto the gold substrate. The cell had an O-ring (ID = 0.6 cm) in the middle through which the laser light contacted the solution. The prism and the cell were mounted on a rotating plate to control the angle of the incident light. A split-field photodiode detector (S2721-02, Hamamatsu) viewed the light reflected from the gold substrate. The photocurrents from two photocells (A and B) on the detector were converted to voltages V_A and V_B by an oscilloscope (TDS 640A, Tektronix). The ratio of the difference to sum signals was obtained numerically by dividing $V_A - V_B$ with $V_A + V_B$. Data were collected by a computer connected to the experimental apparatus using a homemade Labview program. We used the methodology proposed by Tao et al. [15] to convert the voltage ratios into the SPR angle shifts.

2.4. Measurement of metal ion refractive indices

Refractive indices of metal ions were measured using a Spreeta^{TM} sensor (Texas Instruments, Dallas, TX) that has been described in detail by its manufacturer [16,17]. Briefly, the Spreeta^{TM} instrument is a miniaturized RI sensor combining a near-infrared light emitting diode (LED), a gold sensing surface, and an angle-sensitive diode array detector in an integrated device with dimensions 1.5 cm ×

3.0 cm × 4.0 cm. Immediately prior to the measurement, the instrument was calibrated in air and water to be 1.000 and 1.333 RIU, respectively, at room temperature. For the measurement of RIs, one drop of each metal solution (HgCl$_2$, PbCl$_2$, NiCl$_2$, ZnCl$_2$, CuCl$_2$) was put on the Au film. Thereafter, the RIs of each metal ion were monitored for 3 min using the software that the manufacturer provided. The RIs for multiple metal solutions (HgCl$_2$/PbCl$_2$, HgCl$_2$/ZnCl$_2$, HgCl$_2$/PbCl$_2$/NiCl$_2$/ZnCl$_2$/CuCl$_2$, PbCl$_2$/NiCl$_2$/ZnCl$_2$/ CuCl$_2$) were measured with the same procedure after recalibration of Spreeta^{TM} in water.

2.5. Modification of gold substrates

In order to know the saturation time when the gold substrates are fully covered with HDT, in situ SPR measurements were performed. Prior to the adsorption of HDT ethanolic solution on gold substrates, the prism in contact with a gold substrate was rotated to determine the angle where surface plasmon resonance was at a maximum for the cell loaded with ethanol. After the incident angle was fixed at SPR angle, the reflected light detected at cell A and B was then balanced by adjusting the photodetector position until $V_A - V_B$ approached zero. While the reflectance was monitored, the ethanol in a cell was replaced with 1 mM HDT ethanolic solution. The change of SPR signal was initiated by the contact of HDT on gold, and continued until the gold substrate formed the saturated HDT monolayer. Data at the SPR angle were collected every 30 s by a computer.

For the adsorption experiment of metal ions, the detector was moved to a new SPR angle for the HDT-Au under water because it was extremely sensitive to structural and optical properties of the self-assembled layers and loading solutions. The intensities of the reflected light detected at cell A and B were then balanced again by adjusting the photodetector position. While the SPR signal was recorded every three seconds, the water in a cell was replaced with mercury(II). The contact of mercury(II) on HDT-Au initiated the change of SPR signal, and continued until the HDT-Au was saturated with mercury(II). The same procedures were repeated for mercury(II) from 1.0 nM to 1.0 mM, single metal ions (PbCl$_2$, NiCl$_2$, ZnCl$_2$, CuCl$_2$), and multiple metal ions (HgCl$_2$/PbCl$_2$, HgCl$_2$/NiCl$_2$, PbCl$_2$/NiCl$_2$/ZnCl$_2$/CuCl$_2$, HgCl$_2$/PbCl$_2$/NiCl$_2$/ZnCl$_2$/CuCl$_2$). The pHs of all metal solutions were controlled to be pH 4.5 in order to avoid their precipitation by forming hydroxyl complexes, and all experiments were performed at room temperature.

3. Results and discussion

3.1. Refractive indices of metal ions

The SPR spectroscopy is a technique to measure the RIs of molecules at the solid–liquid interface. Table 1 shows RI values for several metal ions. The RIs of each solution con-

Table 1
Refractive indices of metal ion solutions

Metal ions solution		Refractive index[a] (RIU)
Single solution	Hg[II]	1.332889 ± 0.0000065
	Pb[II]	1.333284 ± 0.0000123
	Ni[II]	1.333034 ± 0.0000184
	Zn[II]	1.332842 ± 0.0000124
	Cu[II]	1.332907 ± 0.0000172
Binary solution	Hg[II]/Pb[II]	1.332968 ± 0.0000121
	Hg[II]/Zn[II]	1.332862 ± 0.0000143
Multiple solution	Pb[II]/Ni[II]/Zn[II]/Cu[II]	1.333103 ± 0.0000154
	Hg[II]/Pb[II]/Ni[II]/ Zn[II]/Cu[II]	1.333081 ± 0.0000124

[a] Refractive index of water was calibrated to be 1.333 before the RI measurement of metal ions, and the concentration of each metal ion was 100 μM in water.

taining 100 μM of a single metal are relatively similar although they show different values in the order of Pb[II] > Ni[II] > Cu[II] > Hg[II] > Zn[II]. What makes selective detection difficult is that RIs of mixed solutions are between maximum RI value for Pb[II] and minimum RI value for Zn[II]. Moreover, all solutions are transparent at this concentration, which makes it more difficult to detect a specific ion in an optical way. However, if a specific molecule could be congregated on the solid–liquid interface, its dielectric constant for the layer would be enhanced. The enhanced signal would be detected by the SPR method monitoring not only RI changes of solutions but also thickness changes by molecules adsorbed on the surface. For this purpose, we modified the Au surface with HDT to utilize the characteristics of thiol functional groups that are known to have a specific affinity for Hg[II].

3.2. SPR angle shift by self-assembly of 1,6-hexanedithiol on gold

SPR shift was initiated by the injection of 1 mM HDT ethanolic solution, and it was monitored until the gold substrate was saturated with HDT molecules as shown in Fig. 2. Voltage signals obtained from experiments were converted into angle changed by the equation proposed by Tao et al. [15], and the angles of each time were normalized by the angle at saturation time. The SAM formation is complete within 1 h after exposing the Au substrate to the HDT solution. We also found that SPR angle shift in Fig. 2 follows a first-order Langmuir adsorption model [18,19], which is expressed by the relation

$$\frac{d(\Delta\theta_t)}{dt} = k_a \left(1 - \frac{\Delta\theta_t}{\Delta\theta_{sat}} \right) \tag{1}$$

Here $\Delta\theta_t(t = 0) = 0$, $\Delta\theta_{sat}$ is the final value of $\Delta\theta_t$ corresponding to saturation of SAM adsorption, and k_a is the rate constant of SAM formation on Au. The line in Fig. 2 shows the fit of Eq. (1) to the experimental data (circles). From this fit k_a is determined to be 1.74×10^{-3}/min. As mentioned
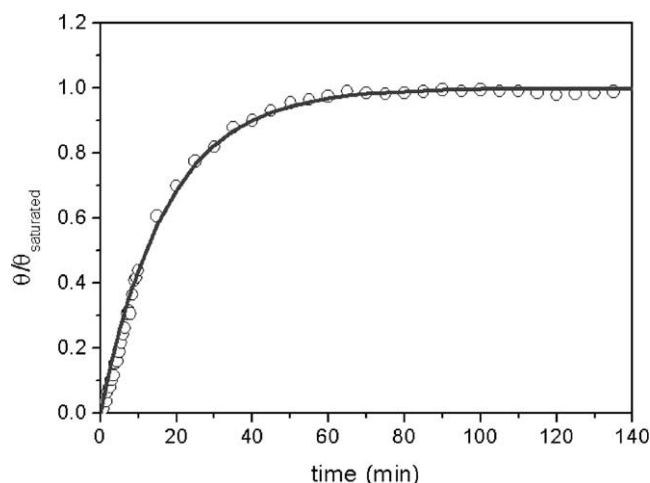
Fig. 2. Normalized time-resolved SPR signal for a 1 mM solution of 1,6-hexanedithiol in ethanol; solid line represents the fit to experimental data (circles) using a first-order Langmuir adsorption model. The rate constant for the fit was estimated to be 1.74×10^{-3}/min. The surface was saturated with HDT in 60 min after injection.

earlier, the SPR angle shift is initiated by the self-assembly and continues until saturation is reached. In other words, $\Delta\theta_{sat}$ corresponds to difference of SPR angles before and after self-assembly.

All the HDT-Au substrates used for the adsorption of metal ions were prepared by the immersion of bare gold substrates into 1 mM HDT ethanolic solution for 3 h for the sufficient self-assembly. They were sequentially rinsed with ethanol and water, and dried with nitrogen gas.

3.3. SPR angle shifts by mercuric ions

The general adsorption equilibrium between Hg[II] in aqueous solution and the HDT-Au surface is established with a ratio of m to n as

$$m\text{Hg}^{2+}(\text{aq}) + n\text{S}(\text{s}) \xrightarrow{K} \text{Hg}_n\text{S}_m \tag{2}$$
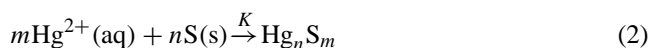
where S is a thiol-saturated HDT-Au surface, and Hg_nS_m is the complex formed on the surface. Then, the adsorption equilibrium constant will be expressed as follows:

$$K_{ad} = K[\text{S}]^n = \frac{[\text{Hg}_n\text{S}_m]}{[\text{Hg}^{2+}]^m} \tag{3}$$

Here the concentration of the complex is proportional to the voltage change (or the SPR angle change). Therefore, Eq. (3) can be expressed as

$$\ln\left(\frac{V_A - V_B}{V_A + V_B}\right) = m\ln[\text{Hg}^{2+}] + \ln\frac{K_{ad}}{k} \tag{4}$$

where k is the correlation constant between the concentration of the complex and the voltage change.

In order to investigate the relation between Hg[II] concentrations and signal changes, voltage changes were investigated on HDT-Au substrates as a function of the Hg[II]
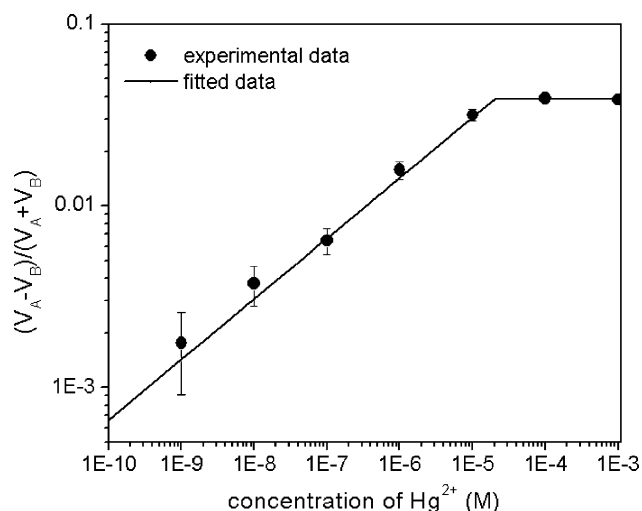
concentration from 1.0 nM to 1.0 mM. The voltage changes were initiated immediately after the Hg[II] solution of 10 nM was injected into the cell, and stopped when no more metal ions attached to the gold surface. Then, more concentrated Hg[II] solutions were injected to cause more adsorption to occur. The voltage changes at stabilized stages for each concentration of Hg[II] were plotted as shown in Fig. 3. They were proportional to Hg[II] concentration up to 10 μM, and steady from 100 μM. The linear fits to the data are expressed as follows:

$$\log\left(\frac{V_A - V_B}{V_A + V_B}\right) = 0.333\log[\text{Hg}^{2+}] + 0.155032$$

$$(1 \times 10^{-9}\,M \leq C \leq 2 \times 10^{-5}\,\text{M})$$

Fig. 3. SPR signal shifts as a function of Hg[II] concentration. Solid line represents the linear fit to the experimental data (solid circles).
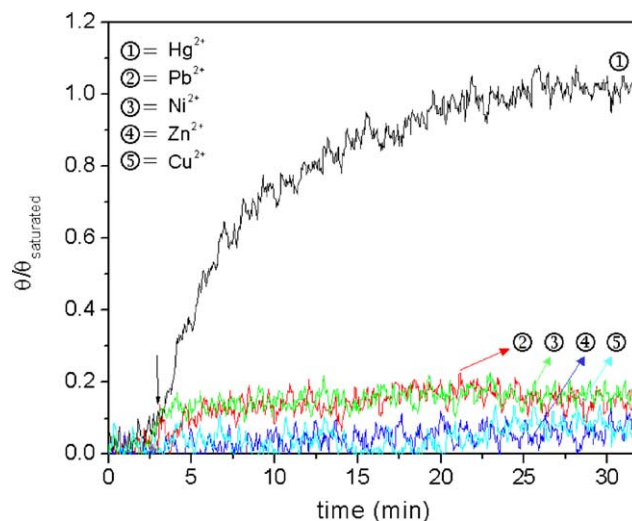

Fig. 4. Normalized time-resolved SPR signals for different metal ions (100 μM each) in contact with the HDT-modified Au substrates. A vertical arrow in the graph indicates the injection time of each metal ion solution.

$$\log\left(\frac{V_A - V_B}{V_A + V_B}\right) = -1.41497 \quad (C > 2 \times 10^{-5}\,\mathrm{M}) \qquad (5)$$

Signal shifts are dependent upon the number of molecules adsorbed on the HDT-Au surface that is illuminated. In other words, the more molecules are on the area, the greater the shift we observe. If the concentration of Hg[II] increases, the number of molecules increases, and consequently the signal changes become larger. However, if the area is fully covered with molecules, no more change occurs in signal. The plot in Fig. 3 notes that the area is fully taken up by molecules when the concentration is around 20 μM. In addition, the first fit in Eq. (5) represents that one Hg[II] ion takes the place of three thiol groups for the adsorption under this condition. It is noted that Hg^{2+} is far less potent than $HgCl_2$ and $HgCl_4^{2-}$ and that the mercury chloride-hydroxyl complex,

$HgCl_4(OH)^{3-}$, is equally potent to noncomplexed mercury chloride, $HgCl_4^{2-}$ [20]. These bulky complexes formed between Hg[II] and hydroxyl groups and chlorides may cause 1:3 adsorption on the HDT-Au surface.

3.4. SPR angle shifts by single metal ions

In situ detection experiments on HDT-Au substrates were performed for single metal solution of $HgCl_2$, $PbCl_2$, $NiCl_2$, $ZnCl_2$, and $CuCl_2$. The concentration of metal ions was fixed at 100 μM from the result of Fig. 3 to make the illuminated area fully covered by molecules and to compare SPR angle shifts at the same amount of each molecule. Fig. 4 is the time-resolved SPR signals for each metal ion, and the data were normalized by the SPR angle at the saturation point of Hg[II]. Each metal solution was injected after 3 min
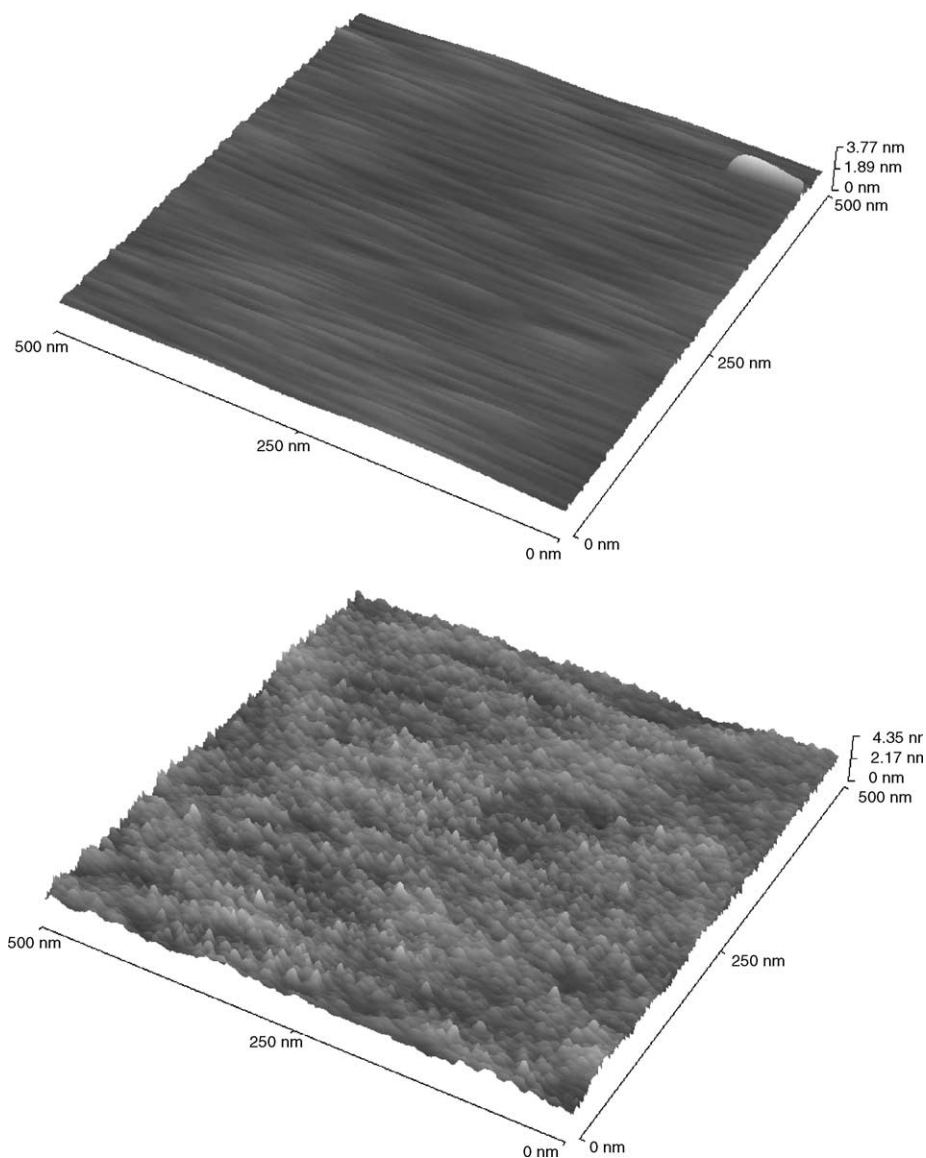

Fig. 5. AFM images of 1,6-hexanedithiol SAM Au substrate (HDT-Au, upper panel) and HDT-Au where mercuric ions were adsorbed (Hg[II]-HDT-Au, lower panel).

stabilization of signals in contact with water. Immediately after the Hg[II] was injected, the signal went up dramatically. On the contrary, other metal ions seldom changed the signals although the signals of Pb[II] and Ni[II] showed comparable shifts to the signals of Zn[II] and Cu[II]. The minute changes might result from the RIs of the metal solutions (Table 1) or a little adsorption of the metal ions on the surface [21].

The morphology of Hg[II]-adsorbed surface was determined by AFM (Topometrix Explorer 2000 scanning probe microscope in the non-contact mode with standard silicon nitride tips, force constant of 0.12 N/m) and compared with that of the HDT-Au surface as shown in Fig. 5. The Hg[II]-modified HDT-Au showed a relatively rough surface compared with the HDT-Au surface. Unquestionably, the adsorption of mercuric ion was enhanced by the modification of Au surfaces with HDT, which increased the SPR angle shifts for this ion.

3.5. SPR angle shifts by multiple metal ions

To examine the selective detection of Hg[II] in mixed metal solutions, the same experiments were done for two binary solutions ($HgCl_2/PbCl_2$ and $HgCl_2/ZnCl_2$) and two multiple solutions ($HgCl_2/PbCl_2/NiCl_2/ZnCl_2/CuCl_2$ and $PbCl_2/NiCl_2/ZnCl_2/CuCl_2$). The SPR signals for those solutions are shown in Fig. 6. The metal solutions were injected after 3 min stabilization of SPR signal under water. The concentrations of metal ions were also fixed at 100 μM, and the plots were normalized by the SPR angle at the saturation point of Hg[II] single solution for comparison. The solutions having Hg[II] induced changes in the SPR signals showing the similar increasing trends as the mercury[II] single solution. On the contrary, the signal for a solution ($PbCl_2/NiCl_2/ZnCl_2/CuCl_2$) containing no Hg[II] hovered around zero. A slight increase in the signal for a
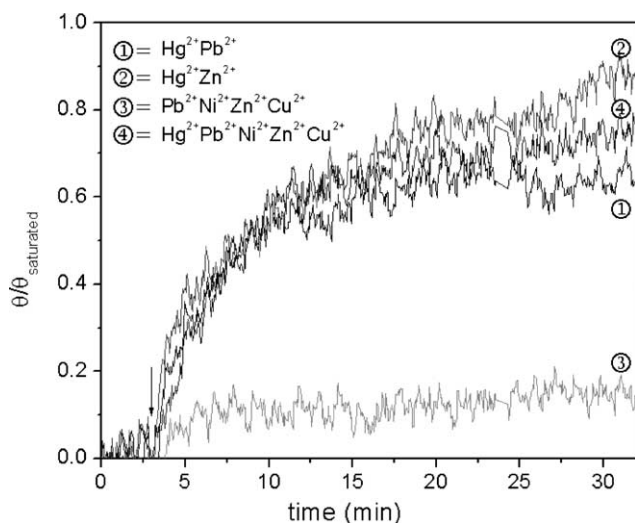

Fig. 6. Normalized time-resolved SPR signals for binary or multiple metal ions on HDT-modified Au substrates. An arrow indicates the injection time of each binary or multiple metal ion solution.

$PbCl_2/NiCl_2/ZnCl_2/CuCl_2$ solution must have resulted from RIs of mixed solution as explained in the single solution experiments. Compared with the SPR change caused by the Hg[II] single solution in Fig. 4, the SPR signals for multiple solutions containing Hg[II] are slightly decreased. The reductions in the saturated SPR shifts are thought to come from the interference by other metals, especially Pb[II] because solutions containing it showed a larger decrease than the $HgCl_2/ZnCl_2$ solution. Nevertheless, the signals for mixed solutions with Hg[II] were markedly differentiated from those containing no mercuric ions. We conclude that we are able to detect Hg[II] selectively in the presence of other heavy metal ions.

We suggest that this selective detection method is a general one. To demonstrate this fact, we coated a gold surface with di-2,4,4-trimethylpentyl phosphinic acid (CYANEX 272), which is known to be a zinc(II)-selective chemical [22]. We obtained preliminary data that the Zn[II] could be selectively detected in the presence of Cd[II] using this SPR method (data not shown here). The sensitivity of the Zn[II] sensor, however, was less than that of the Hg[II] sensor. It is thought to result from a uniformity of the CYANEX 272 layer for Zn[II] sensor or the structure of existing molecule. The HDT are bonded on the Au surface chemically whereas the CYANEX 272 is attached by physical attraction, such as van der Waals forces, which makes it difficult to form a uniform monolayer. We prepared a CYANEX 272-Au layer after contacting an Au surface with CYANEX 272 and sequentially drying it in an oven at 80 °C, which might cause the production of an irregular or thick layer. The thickness control and uniformity of the film will be key factors to determine the sensitivity in designing other metal sensors, and special techniques such as Langmuir–Blodgett deposition, dip-coating might be needed to accomplish this goal. The structure of existing molecules in solution is another important factor to determine the sensitivity of the sensor. We calculated the composition of molecules of metal solutions using MINEQL+ (Environmental Research Software, ME). We find that 99.5% of zinc exists as a form of ion (Zn^{2+}) whereas most of mercury exists as complex forms such as $HgCl_2$, $HgCl^+$, $Hg(OH)_2$ (aq), and HgClOH (aq). The existence of bulk complexes supported not only the high sensitivity for the Hg(II) sensor but also the 1:3 adsorption between mercury and the HDT-Au by steric hindrance.

Regardless of the selective detection for different metal ions, this technique is judged to have room for the improvement because of the slow rate for detection. Remarkable changes in SPR signals occur about 2 min after injection, but it takes about 30 min for these changes to reach a steady-state (saturation). This fact is an undoubted disadvantage compared to the detection speed of AA or ICP. The cell used for the experiments was a batch cell. Therefore, the adsorption was diffusion-limited. We expect that the fabrication of a microfluidic flow cell would not only solve this problem but it would also reduce the amount of waste, and this pos-

sibility is being studied in our laboratory for more practical applications.

4. Conclusions

We have demonstrated a Hg[II]-selective optical detection method that uses the SPR technique after modification of an Au surface with 1,6-hexanedithiol. The HDT-modified Au surface (HDT-Au) promoted the adsorption of mercuric ions and enhanced changes in the SPR signals, which were detected using a split photodiode. We could quantify in solution the concentration of Hg[II] from 1.0 nM to 1.0 mM. Mercuric ions become attached to thiol molecules on HDT-Au with the adsorption equilibrium ratio of 1:3 up to 20 μM at which point the area illuminated by the incident light became saturated. At still higher concentrations the SPR signal did not change. In situ SPR experiments on HDT-Au with different heavy metal ion solutions (100 μM) enabled us to differentiate Hg[II] from Pb[II], Ni[II], Zn[II], and Cu[II], although each solution was transparent at that concentration and the refractive index of each solution was nearly the same. AFM data supported the conclusion that mercuric ions are preferentially adsorbed by the HDT-Au surface. The phenomena were reproduced in solutions containing two or more heavy metal ions although the SPR signals for mercuric ions in mixed solutions were slightly less than the value in solutions containing only Hg[II] owing to interference from the other metal ions. Consequently, Hg[II] could be selectively detected by optical means in the presence of other heavy metal ions over a wide range of concentrations.

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