Fabrication of reusable sensor for detection of Cu^{2+} in an aqueous solution using a self-assembled monolayer with surface plasmon resonance spectroscopy†

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The proposed procedure for recycling the sensor surface consists of (1) the self-assembly of 2-aminoethanethiol hydrochloride (AET) on the Au substrate, (2) the neutralization of zwitterion-like species, $–NH_3^+Cl^−$ to $–NH_2$ by treatment with a NaOH solution (pH 11), (3) the detection of Cu^{2+} on the NaOH-treated AET–Au substrate, and finally (4) regeneration of the sensor surface from [$–NH_2 \rightarrow Cu^{2+}$] to [$–NH_3^+Cl^−$] by treatment with 1 M HCl.

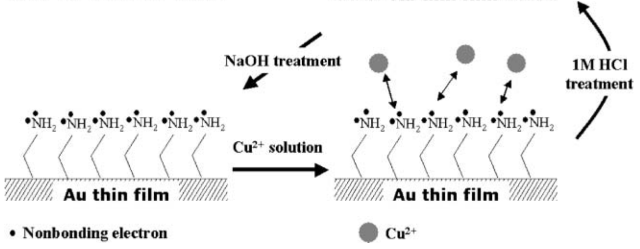
The detection and measurement of heavy metal ions present in aquatic streams are of great importance in assessing environmental damage and possible strategies for remediation. Several methods are available for determining heavy metal ions concentration and include polarography, atomic absorption (AA) and inductively coupled plasma (ICP) spectroscopy. In spite of the fact that some of these techniques are rapid and precise, recent analytical interest has focused on developing optical sensors that can be reused and do not involve the destruction of samples. They also have the advantages of size, cost-effectiveness, simplicity, no need for a reference solution, and can be used in the field.[1,2] Optical sensors developed to date, however, require the use of tagging agents or carriers having a selective affinity for the target metal ion of interest. In contrast, it is well known that surface plasmon resonance (SPR) spectroscopy is an optical sensor that does not require tagging agents.[3–5] Although SPR measurements for use in the detection of specific interactions of biomolecules have been studied extensively,[6–10] the selective detection of heavy metal ions by SPR has been much less extensively studied, because it is difficult to detect a specific heavy metal ion due to the similar refractive indices and optical transparency when diluted. The complexation of Cu^{2+} with polyacrylic film has been studied by SPR measurement.[11a] For the fabrication of a heavy metal ion sensor, the use of a peptide-modified sensor surface for Cu^{2+} detection and a thiol-terminated self-assembled monolayer (SAM) for Hg^{2+} analysis with SPR measurement has been reported.[11b,12] However, the former method involves multiple steps to generate the sensor surface and, in the latter case, it is difficult to regenerate the sensor surface due to the strong interaction between thiol functional groups and Hg^{2+}. These results clearly suggest that, in order to make the SPR measurement of heavy metal ions more feasible, the facile preparation of a sensor surface and its subsequent regeneration, including sensitivity and selectivity are necessary.

In this study, we demonstrate the selective detection of Cu^{2+} in the range of 0.1 μM to 1.0 mM by combining an SPR measurement with a reusable sensor surface comprised of a relatively simple amino-terminated self-assembled monolayer as a molecular recognition element.

The overall experimental procedures are summarized in Scheme 1. The SAM of 2-aminoethanethiol hydrochloride (AET) on the Au thin film was formed by treatment with a 1 mM AET ethanolic solution for 18 h.[13] The formation of an AET monolayer was investigated by SPR measurements and Auger electron spectroscopy (AES). Although the SAM of the AET was formed on the Au surface, after the long equilibration time (18–24 h) of the AET SAM with Cu^{2+} (that is, the adsorption of Cu^{2+} to the AET SAM on the Au thin film was assumed to be completed), no distinguishable change in θ_{SPR} was observed. This suggests that little interaction occurs between the initially formed AET SAM and Cu^{2+}. This phenomenon can be attributed to the absence of nonbonding electrons in "nitrogen" atoms, which plays a critical role in the complexation with Cu^{2+}. The initially formed AET SAM was assumed to be a zwitterion-like species, $–NH_3^+Cl^−$. Therefore, in this study, through the NaOH treatment, we were able to change the terminal functional group from $–NH_3^+Cl^−$ to $–NH_2$ by the removal of H^+.

$$RNH_{3\ surface}^{+} \xleftrightarrow{pK_a} RNH_{2\ surface} + H_{solution}^{+} \qquad (1)$$

We focused our attention on the detection of changes in the optical properties of the SAM layer as a result of the



Scheme 1 Schematic representation of the experimental procedures for fabricating a recyclable and selective Cu^{2+} SPR sensor surface.

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† Electronic supplementary information (ESI) available: Experimental procedures and details. Stratified structure of an SPR system (Fig. S1), incident angle SPR contour plot for AET SAM (Fig. S2). See http://www.rsc.org/suppdata/cc/b5/b504064g/index.sht

deprotonation and reprotonation of the AET SAM layer. It would be expected that these changes in surface charges would affect both the electronic configuration and the orientation of the AET SAM layer.[14a] This would result in a change in the dielectric function and, hence the refractive index, $n = (\varepsilon)^{1/2}$, of the AET SAM. For *in situ* SPR measurements of the AET SAM ionization, it was necessary to induce deprotonation in the same experimental cell where the AET SAM was formed on the Au thin film. We proceeded to examine the pH-dependent ionization behavior of a formed AET SAM using time-resolved SPR measurements. The pK value of surface bound $HS(CH_2)_2NH_2$ was assessed to be about 5.3.[14b] The Au thin film modified with the AET SAM layer was introduced into the aqueous solution (pH = 3) and the $\Delta R(t)$ behavior of this system was monitored in real time (as in Fig. 1B). At a sufficient time after the immersion (the moment that ΔR was considered to settle at its time-independent value), at time t_o, we changed the pH of the solution to 11. Following the subsequent stabilization of the SPR angle, the pH of the solution was again changed to 3. The results for two such cycles of pH alterations are presented in Fig. 1B. The arrows indicate the instants when the solution pH is changed by the injection of HCl or NaOH into the experimental cell. A definite trend in variation, above the experimental noise level and following the sequence of pH changes, was observed for the $\Delta R(t)$ data (symbols) of Fig. 1B. The line through the data represents this trend. Interestingly, it was also found that exactly the opposite trend in the variations in $\Delta R(t)$ seen in Fig. 1A was observed when the pH-dependent SPR measurements of Fig. 1B were repeated using the AET SAM-free Au thin film, with all other experimental conditions being unchanged. Therefore, it is obvious that the observed pH-dependent changes in SPR reflectance in Fig. 1B are due to morphological changes in AET SAM caused by deprotonation and reprotonation. The SPR angle increases when AET is protonated in an acid environment, and the reverse situation is observed in the case where a base solution is used. The accurate measurement of these parameters is currently underway to focus, in particular on the careful determination of the AET SAM packing density. Nevertheless the above-estimated values permit an overall description of the optical response of an AET modified surface to deprotonation–reprotonation and also provide convincing evidence for the change of $–NH_3^+Cl^-$ to $–NH_2$ as the result of the NaOH treatment.

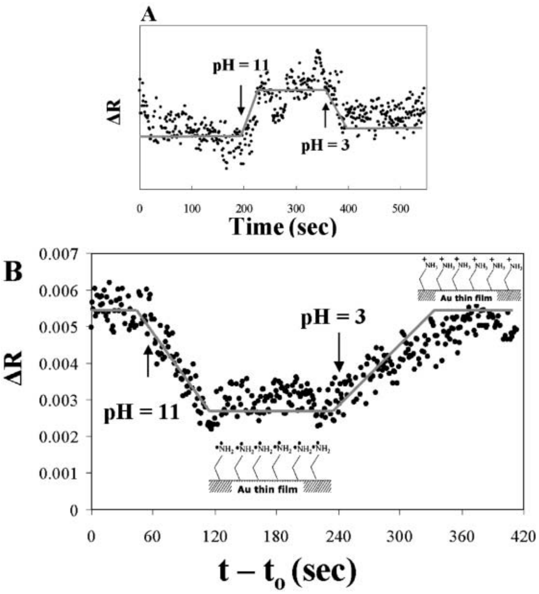

Fig. 1 Effects of changing the solution pH on the SPR angle for a five-phase multilayer structure including (A) SAM-free Au film and (B) a completely formed SAM of AET on Au film. After the AET SAM is formed in an ethanolic solution of 1 mM AET, the AET–Au surface is dried with N_2 and allowed to stabilize in an aqueous solution at pH 3 for t_o ($\sim$10 min). At $t > t_o$, the solution pH is again changed to between 11 and 3. The symbols represent experimental data, and the arrows indicate the points in time when NaOH (at $t - t_o = 60$) or HCl ($t - t_o = 240$) is introduced into the cell to change the solution pH. The line through the symbols shows the general trend for the variations in ΔR. The inset figures represent the corresponding surface status.

The general adsorption equilibrium between Cu^{2+} in aqueous solution and the AET–Au surface is established with a ratio of m to n as

$$mCu^{2+}(aq) + nN(s) \xrightarrow{K} Cu_mN_n \tag{2}$$

$$K_{ad} = K[N]^n = \frac{[Cu_mN_n]}{[Cu^{2+}]^m} \tag{3}$$

where N is an amino-terminated AET–Au surface, and Cu_mN_n is the complex (multi-dentate) formed on the surface. The adsorption equilibrium constant can then be expressed as equation (3). Here the concentration of the complex, which can be approximated as the surface coverage, is proportional to the angle shift, $\Delta\theta_{SPR}$.[12,15] Therefore, equation (3) can be expressed as

$$\ln(\Delta\theta_{SPR}) = m\ln\left[Cu^{2+}\right] + \ln\frac{K_{ad}}{k} \tag{4}$$

where k is the correlation constant between the concentration of the complex and $\Delta\theta_{SPR}$. The SPR angle shifts are dependent upon the number of Cu^{2+} adsorbed to the AET–Au surface. In other words, the more Cu^{2+} that are adsorbed to the AET–Au surface, the greater will be the observed angle shift. Fig. 2 shows the $\Delta\theta_{SPR}$ on AET–Au substrates as a function of Cu^{2+} concentration in the range of 0.1 μM to 1.0 mM. The maximum value of Cu^{2+} levels permitted by EPA is 1.3 ppm (this value corresponds to *ca.* 0.02 mM Cu^{2+} solution). Therefore the working range of 0.1 μM to 1.0 mM for Cu^{2+} detection is reasonable for the purpose of practical applications.

The slope ($m = 0.27$) in the linear fit of equation (4) indicates that one Cu^{2+} ion takes approximately the place of 3.7 "nitrogen" atoms for complexation under the given conditions. Considering the fact that four of the N donor atoms in the functional groups are usually coordinated with Cu^{2+},[16] this result is in good agreement with the theoretical prediction. Fig. 2 also shows that the concentration of Cu^{2+} in the aqueous solution can be quantitated within the concentration range of 1×10^{-7} M – 1×10^{-3} M by a linear interpolation.

To use AET-modified SPR sensors for practical analysis, a number of factors must be addressed in addition to sensitivity, detection range and reproducibility. These include any possible interference from other metal ions in actual samples and the reusability of the sensing surface. To investigate the selectivity of the AET-modified SPR sensor, the divalent cations Ni^{2+} and Zn^{2+}

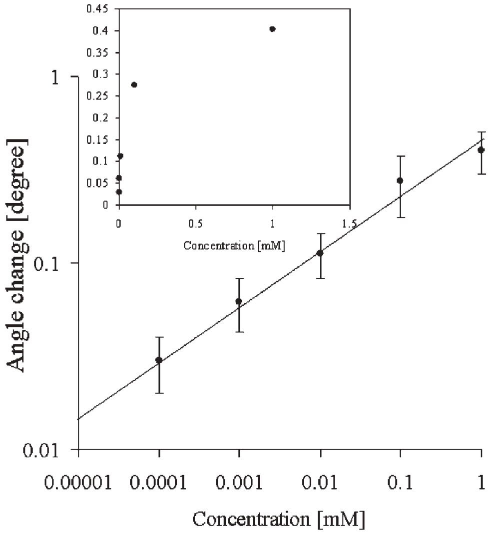

Fig. 2 SPR angle shifts of the AET–Au surface as a function of Cu^{2+} concentration (pH 5). Bars correspond to standard errors of triplicate samples.

were selected as adsorptive competing ions with Cu^{2+}, because those cations are divalent and have similar ionic radii. Specifically, Ni^{2+} is known to seriously interfere with Cu^{2+} detection (and *vice versa*) since both ions form square planar 4N complexes with a "nitrogen" containing functional group.[17] More specifically, Ni^{2+} has a similar hydrodynamic radius, ionic mobility, and limiting ionic conductivity to Cu^{2+}. As can be seen in Fig. 3A, 1 mM of Ni^{2+} and Zn^{2+} on the AET Au thin film produces an SPR response that is about one tenth and one fifth, respectively, of the response obtained for Cu^{2+} with the same concentration. In the case of mixtures consisting of Ni^{2+}, Zn^{2+}, and Cu^{2+}, $\Delta\theta_{SPR}$ gives a similar result (arrow in Fig. 3A) for the homoionic adsorption of Cu^{2+}. Therefore, we conclude that the AET-modified SPR sensor is able to selectively detect Cu^{2+} in the presence of Ni^{2+} and Zn^{2+}.

The regeneration (reusability) of the sensor surface for further use is also an important concern that can determine the economic feasibility of sensor chips. Concerning the reusability of the sensing surface (Au film), it was observed that it is possible to regenerate the AET-modified surface by treatment with 1 M hydrochloric acid for 2 min and to obtain a similar optical response as shown in Fig. 3B.

In summary, a facile method for analyzing Cu^{2+} in aquatic medium by combining the SPR measurement with a recyclable sensor surface of AET SAM is proposed. From the results, both the NaOH and HCl treatment of the AET SAM on the Au thin film are essential to accomplish the selective and recyclable sensor surface for the detection of Cu^{2+}. Compared to other techniques, such as atomic absorption spectrometry, our SPR sensors are simple, low cost, and, as a result, we believe that the SPR sensor may be a good alternative for detecting Cu^{2+} in drinking water.

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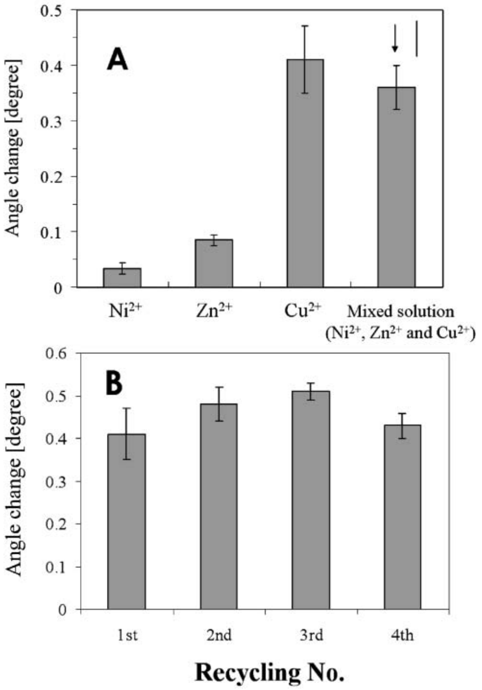

Fig. 3 (A) SPR angle shifts of the AET–Au surface after the homoionic adsorption of 1 mM (pH 5) Ni^{2+}, Zn^{2+}, and Cu^{2+}, respectively. The arrow indicates the SPR angle shift obtained from ternary metal ion solutions (pH 5) consisting of 1 mM Ni^{2+}, Zn^{2+}, and Cu^{2+}. Bars correspond to standard errors of triplicate samples. (B) The regeneration of Cu^{2+} adsorbed AET Au thin film after treatment with 1 M HCl for 2 min. Bars correspond to standard errors of triplicate samples.

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