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Dyes and Pigments 44 (2000) 55–61

DYES and PIGMENTS

A self-assembled squarylium dye monolayer for the detection of metal ions by surface plasmon resonances

Sung-Hoon Kim [a,*], Sun-Kyung Han [a], Jae-Ho Kim [b], Myung-Bock Lee [c], Kwang-Nak Koh [d], Shin-Won Kang [d]

[a] *Department of Dyeing and Finishing, College of Engineering, Kyungpook National University, Taegu, 702-701, South Korea*
[b] *School of Chemical Engineering and Biotechnology, Ajou University, Suwon, 442-749, South Korea*
[c] *School of Electronics and Electrical Engineering, Kyungpook National University, Taegu, 702-701, South Korea*
[d] *Sensor Technology Research Center, Kyungpook National University, Taegu, 702-701, South Korea*

Received 20 May 1999; accepted 12 July 1999

Abstract

Self-assembly of a squarylium dye containing an alkanethiol substituent on a gold surface is described. The self-assembled monolayers (SAMs) obtained were investigated by contact angle measurement and atomic force microscopy (AFM). Surface plasmon resonance (SPR) has been employed to investigate the interaction of the squarylium dye monolayer on gold with metal ions. A highly Cu^{2+} selective SPR sensing system was demonstrated with SAM for the squarylium dye on gold. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Surface plasmon resonance (SPR); Squarylium dye (SQ); Cu^{2+} ion sensor; Resonance angle; Self-assembled monolayer (SAM)

1. Introduction

Self-assembled monolayers (SAMs) on metal surfaces have received much attention because of the importance of establishing how surface properties can be altered by light and how the behavior of an SAM is affected by its structural rigidity [1,2].

A particularly important type of monolayer self-assembly occurs when a gold substrate contacts a suitable organosulfur compound [3,4]. This results in a surface adsorbed monolayer possessing well-defined chemical and physical properties, which have been characterized by external reflection infrared spectroscopy (FTIR-ESR), contact angle goniometry, X-ray photoelectron spectroscopy (XPS), electrochemical method, ellipsometry, atomic force microscopy (AFM) and other techniques [3].

Such assemblies could provide a means to control the chemical and physical properties of interfaces for a variety of heterogeneous phenomena, including catalysis [5], corrosion [6], lubrication [7] and adhesion [8]. The ability to control interfacial processes has important implications from the point of view of both fundamental and technological advances.

Although squarylium dyes exhibit a sharp visible absorption in solvents, their absorption in the

* Corresponding author. Tel.: +82-53-950-5641; fax: +82-53-950-6617.
E-mail address: shokim@bh.kyungpook.ac.kr (S-H. Kim)

PII: S0143-7208(99)00071-6

solid state is panchromatic and very intense [9]. This class of dyes has attracted much attention because of their potential application in xerographic organic photoreceptors [10], optical recording media [11] and organic solar cells [12], on account of their advantageous properties such as photoconductivity and their sharp and intense absorption in the visible or near infrared regions [13]. We have previously reported the synthesis [14], electrochromic properties [15] and metal ion sensing [16] of squarylium dyes containing an indoline moiety.

We have also reported the synthesis and self-assembly of a new squarylium dye containing an alkanethiol moiety with an amide group incorporated into the backbone. We concluded that the presence of the amide group in the chain provided orientational stability through intermolecular hydrogen bonding within the monolayer, thus enhancing the mechanical durability of the SAM [17].

The purpose of the present study is to investigate the surface properties of the squarylium dye monolayer on gold, by use of AFM and contact angles, which were a sensitive probe of the structure of the surface.

Surface plasmon resonance (SPR) has been recently demonstrated as an effective optical technique for chemical sensing. A number of SPR configuration systems have been reported, such as immunoassay [18], liquid [19], gas [20], and thin film [21]. A surface plasmon is a surface charge-density wave at a metal surface. As is well known, surface plasmon can be excited by the attenuated-total-reflectance (ATR) method proposed by Kretschmann [22].

Since the resonance angle is very sensitive to variations in the refractive index of the medium just outside of the metal thin film, the refractive index of a film, e.g. multilayer Langmuir–Blodgett film [23] or polymeric film [24] is obtained by the surface plasmon technique.

The measurement of the refractive index of a bulk chemical sample can be used to determine the concentration of an analyte, assuming that the refractive index of solution depends solely on the analyte concentration. This can be performed by employing selective chemical sample sensing layers (e.g. selective membrane, chromoionophore, specific binding layer, etc.). The chemical sensing layer implies a thin film, which has optical properties as a function of the concentration of the analyte to be sensed.

We also report here the development of Cu^{2+} ion sensor and demonstrate that SPR is capable of sensing Cu^{2+} ion using a squarylium dye containing self-assembled monolayer on gold.

2. Experiment

2.1. Contact angle measurements

For the evaluation of surface wettability, the water contact angles of the gold, cystamine–gold and SQ dye–cystamine–gold were measured at room temperature using a contact angle goniometer (Model G-I type, Erma Inc., Tokyo, Japan) [25]. A droplet of water was placed on the air-side surface of a film at 25°C, and after 30 s the contact angle was measured. More than 10 times measurements were carried out for a single sample and the values obtained were averaged (Fig. 1a).

2.2. AFM analysis

The topographic images of the sample surfaces were collected in the contact mode using a NanoScope III STM manufactured by Digital Instruments.

The silicon nitride cantilevers had a nominal spring constant of about 0.06 N/m and scanning parameters were adjusted to obtain the clear images revealing the effects of SAMs on deposited Au surfaces.

2.3. Preparation of self-assembled monolayer

The gold surface was prepared by electron-beam evaporation of 30 Å of nickel–chromium as an adhesion promoter, followed by 500 Å of Au, onto the glass slide. Stepwise chemical assembly of squarylium dye monolayer was effected by the covalent linkage of the carboxyl unit of the SQ dye to a cystamine-monolayer-modified gold surface.

The SQ dye was prepared using previously described procedures [17]. The Au deposited glass

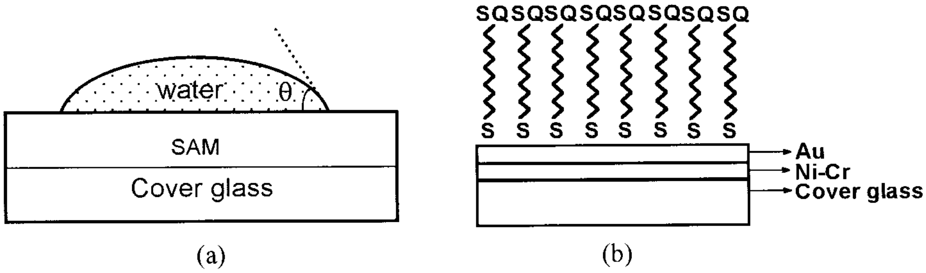

Fig. 1. Schematic representation of (a) a water droplet on a solid substrate and the contact angle, θ. (b) a multilayer system of SPR sensing element (SQ: squarylium dye).

slide was immersed in 1×10^{-2} M cystamine hydrochloride aqueous solution for 2 h and then rinsed with deionized water. After rinsing, the cystamine adsorbed gold layer was treated with 1×10^{-2} M ethanolic solution of 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (ECD) and 5×10^{-4} M of SQ dye for 12 h. The resulting monolayer was rinsed several times with deionized water and dried out using N_2.

2.4. Surface plasmon resonance (SPR) measurements

The squarylium dye-containing SAMs on gold as a sensor chip and prism ($n=1.515$, Sigma, BK7) were loaded on the sample solution cell by a micrometer. Optical contact between the prism and this sensor chip was achieved by a refractive index matching fluid ($nD=1.151\sim1.517$, Merck). The polarized incident light from the laser diode (4.5 mW, 670 nm) via the prism was reflected and detected by the photo diode detector (ANDO Electric Co. Ltd., AQ-1976) with a multi-meter(ANDO Electric Co. Ltd., AQ-1135E). The intensity of reflected light was detected changing the incident angle of polarized light. This angle was regulated by the automatic-motorized rotary stage controller with a resolution of 0.004°.

The incident angle which showed the smallest optical reflectance varied with the change of the Au surface dielectric constant, due to the interaction between the SQ dye sensing membrane with a metal ion. Fig. 1b shows the principal construction of the sensing chip. Various concentrations of metal ions ($M^{n+}(NO_3)_n$, $=Cu^{2+}$, Ag^+, K^+, Na^+, Zn^{2+}) ranging from 1×10^{-4} to 1×10^{-12} M (in Tris–HCl buffer, pH = 7.0, 0.1 M) were prepared to measure the intensities of reflected light and their resonance angle shifts. All the sample solutions were flowed into the sample cell from low concentration and the sample cell was washed with a buffer solution before measuring the different sample by pumping. The experimental set-up is shown in Fig. 2.

3. Results and discussion

A general synthetic strategy for the preparation of a squarylium-alkanethiol containing an amide bond has been developed [17]. The monolayer precursor required for the present study was synthesized in several steps. Stepwise chemical assembly of a squarylium monolayer on gold was performed by covalent linkage to a cystamine-monolayer–modified gold. A cystamine monolayer was first assembled onto a gold surface. The SQ dye was coupled to the base monolayer as recently described [26]. The self-assembled monolayer was prepared on a gold surface for this study, and is shown in Fig. 3.

The most compelling evidence for intermolecular hydrogen bonding within the monolayer was obtained by using FTIRRAS (Fourier transform infrared reflection adsorption spectroscopy). A general broadening of the amide stretch appearing near 3300 cm^{-1} was taken to be indicative of the presence of intermolecular hydrogen bonding within the SQ dye-containing SAM. Substrates with different surface energies can be fabricated readily by introducing appropriately functionalized organosulfur reagents to the gold surface, which leads to a well-defined alkanethiol monolayer [27].

Specifically, the surface energies can be adjusted systematically from hydrophobic to hydrophilic simply by varying the polarity of the tail group of the thiol adsorbates. The spreading of fluids over solid substrates is a ubiquitous process of fundamental technological importance. Wetting and spreading play a critical role in applications such as coatings, cosmetics, lubrication, etc. [28].

The water contact angles of gold, cystamine–Au (Au I), and SQ–cystamine–Au (Au II) are shown in Table 1.

The contact angle measurements showed that surface-modified Au I and Au II were more hydrophilic than that of a gold surface. Au I had a contact angle of 78°, indicating that the surface containing amine groups are very polar. The decreased contact angle observed in Au II can be rationalized by the structure of the SQ dye-SAM. The conjugated terminal groups, $C{=}N^+$ and $-O^-$, of the SQ dye of SAM are more hydrophilic, and thus have smaller water contact angles than Au II. More detailed information on the surface structure and the direct image of the self-assembled SQ dye monolayer on the gold surface can also be obtained with AFM. Topographic images of the SAMs were collected over large regions of

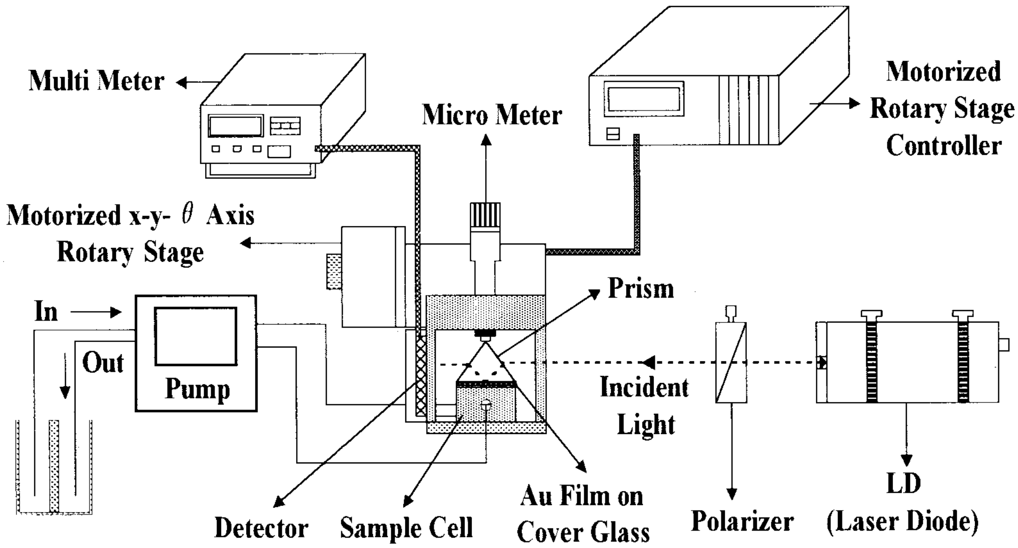

Fig. 2. Diagram of SPR-based chemical sensor system.

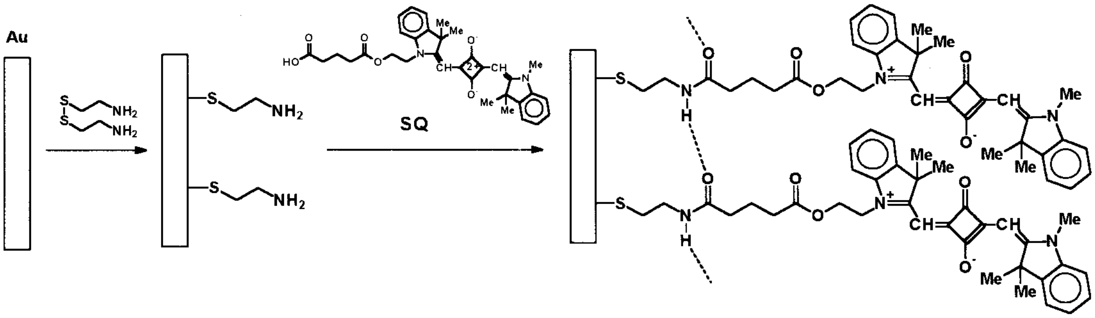

Fig. 3. Stepwise organization of SQ dye monolayer on Au.

Table 1
Water contact angle of surface-modified Au

Substrates	Contact angle (°)[a]
Bare gold	83 ± 2
Au I	78 ± 3
Au II	70 ± 1

[a] Measured by contact angle goniometer.

the surface (100×100 nm) by detecting the normal deflection of the cantilever as a function of the position across the sample.

Fig. 4 shows the AFM images of (a) bare gold surface, (b) cystamine monolayer and (c) SQ dye monolayer linked to cystamine.

Since the gold surface was prepared by electron-beam evaporation onto cover glass, the topography image of the gold surface does not have a flat shape. The mean value of height from cross-sectional analysis, roughness of the surface, is about 1.38 nm [Fig. 2(a)]. The image of the cystamine deposited surface onto the gold surface shows a small globular shaped structure and the mean valence is 4.04 nm [Fig. 4(b)]. Fig. 4(c) on the other hand shows a surface topography that has a much greater grain size, and a lumped shape rather than a cystamine deposited surface. The mean value of the SQ dye monolayer is 4.53 nm. These direct AFM images provide evidence of SAM formation by stepwise chemical assembly.

Surface plasmon resonance (SPR) is a widely known optical technique for studies of thin films and interfaces, as well as biological and chemical sensing. With the introduction of commercial SPR biosensors [18], SPR has become increasingly popular as a tool for the qualitative and quantitative sensing of interactions between biochemicals. SPR is observed as a sharp dip in the dependence of the intensity of p-polarized light reflected from the metal film on the light spectrum or on the

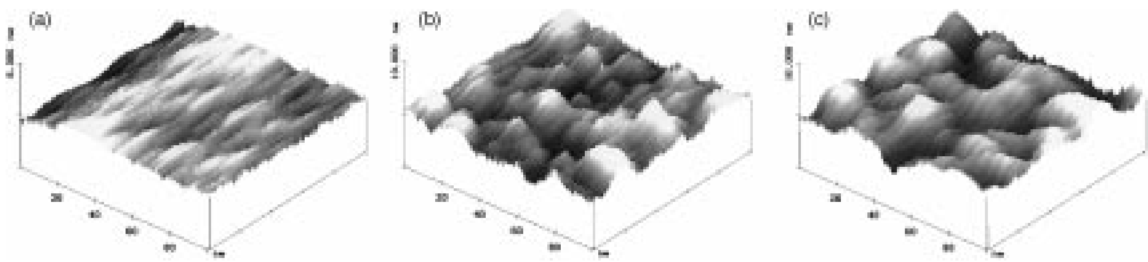

Fig. 4. Atomic force microscope images of the film surface. (a) bare gold, (b) cystamine-gold, and (d) SQ dye-cystamine-gold.

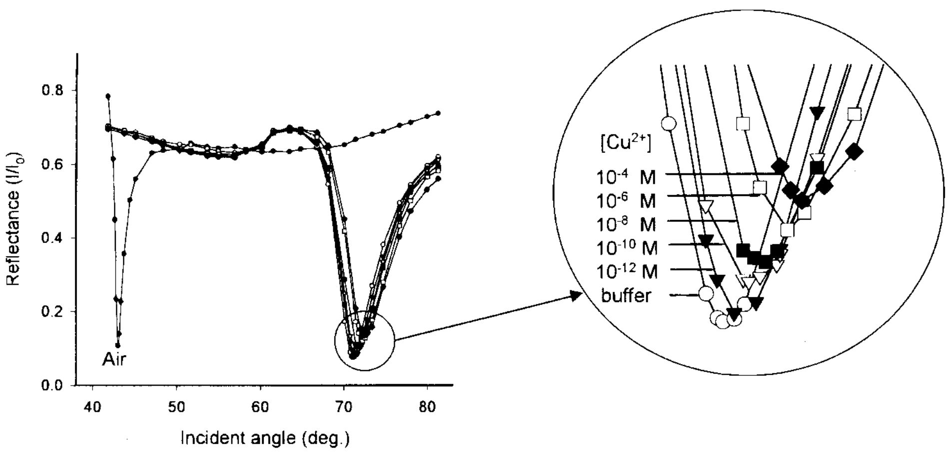

Fig. 5. Effects on SPR waves of coating a gold film with a sensing membrane containing SQ dye.

angle of the light incidence. In the most frequently used SPR biosensors, binding of the reactants are recorded as a shift of the angular position of the reflected intensity minimum.

A highly selective ion sensing SPR for the determination of metal ions was prepared with a plasticized PVC-PVAc-PVA membrane containing a dithioaquarylium dye (DTSQ) [29]. In the results, DTSQ showed a striking selectivity for Ag^+. In the surface plasmon method, the resonance angle is very sensitive to variation of the refractive index of the medium outside the metal film. When the medium outside SAM of the squarylium dye is changed from air to buffer solution, the resonance angle changed from 42.96 to 70.67, as shown in Fig. 5. Fig. 5 shows the SPR curves for gold coated with a film of squarylium dye–cystamine as a function of Cu^{2+} concentration; as the Cu^{2+} concentration increases, the resonance angle also increases.

Fig. 6 shows that the addition of other metal ions such as Ag^+, Zn^{2+}, Na^+ and K^+ up to 1×10^{-4} M does not have any significant effect of the shift in the resonance angle. For the sensor system, a linear response range was achieved for the Cu^{2+} ion between about 1×10^{-12} to 1×10^{-4} M. Owing to the trace detection and specific resonance to Cu^{2+} in SPR, the SAM of the squarylium

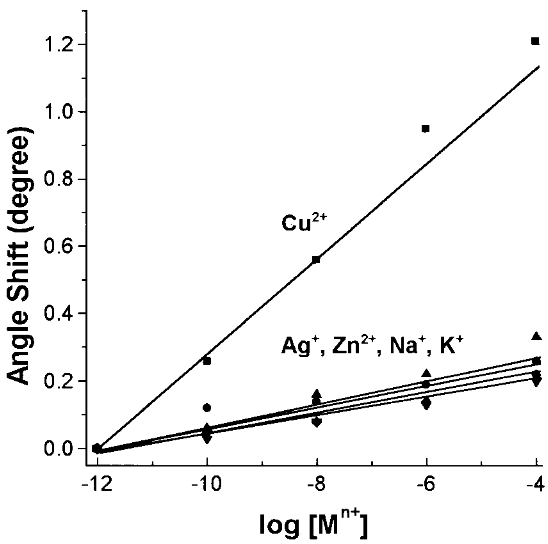

Fig. 6. Calibration plots for metal ions obtained with SPR.

dye appears to be potentially suitable for practical SPR sensor application.

Acknowledgements

The authors acknowledge the financial support of the Korea Research Foundation made in the Program year 1998 (Grant to S.H.K., S.R.K. and C.M.Y.).

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