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Photoinduced refractive index change of self-assembled spiroxazaine monolayer based on surface plasmon resonance

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Abstract

The self-assembly of a photochromic, spiroxazine-containing alkanethiol monolayer on a gold surface is described. Contact angle measurements confirm the presence of a hydrophilic surface in the self-assembled monolayer. Atomic force microscopy (AFM) images and measurements confirm that this monolayer was formed by stepwise chemical assembly. Evidence for self-assembled monolayer-photochromism was gathered from UV–visible spectral evaluation before and after irradiation at 366 nm. Surface plasmon resonance (SPR) revealed that a resonance angle change of 0.13° which corresponded to a refractive index change, Δn, of 0.0034. © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Self-assembled monolayer; Spiroxazine; Refractive index change; Surface plasmon resonance; Alkamethiol

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1. Introduction

Surface plasmon resonance (SPR) phenomenon can be used to measure the refractive index of a wide variety of chemical samples. Many optical sensing systems have been developed that link the sensitivity of SPR to the refractive index of bulk and thin-film dielectrics and to the thickness of thin films. Such a refractive index determination may be utilized as a process-control and/or monitoring tool in chemical systems that can be qualified by an acceptable refractive index window. A number of SPR configuration systems have been reported which have been used in the study of immunoassays [1] and in the evaluation of liquid [2] configurations, gaseous [3] assemblies and thin film [4] properties.

Surface plasmon waves (SPWs) are excited at the interface between a thin, highly reflecting metal layer (e.g. silver or gold) and the sample by coupling through a substrate with a high-refractive index, as illustrated in Fig. 1a (Kretschmann configuration). SPWs are transverse waves with an oscillating electric field that lies normal to the surface.

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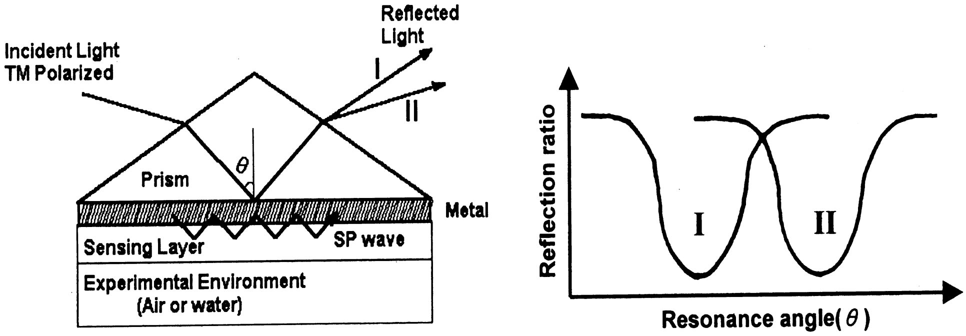


Fig. 1. (a) The Kretschmann configuration. (b) SPR-reflectance waves. The light reflectance is recorded as a function of the angle of incidence (θ).

Since surface plasmons only have an electric field component normal to the surface, *p*-polarized light is required to satisfy the boundary conditions necessary to excite SPR. At the surface plasmon resonance angle, the energy of the metal surface coincides with the incident photon and the charge density wave. The photon energy is then transferred to the SPW, which results in energy loss from reflected intensity. This phenomenon can be observed as a sharp dip in the reflected light intensity (Fig. 1b).

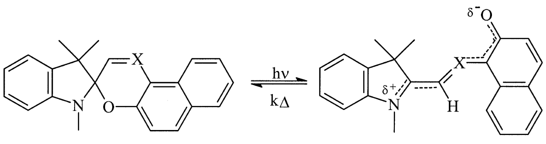
Outside the metal an evanescent electric field exists. This evanescent wave is part of the internally reflected light beam and partially penetrates into the lower refractive index medium. The evanescent wave can interact optically with compounds that are close to the surface or at the surface. Changes in the optical properties of this region will influence the SPR angle. This accounts for the usefulness of SPR for chemical sensing and optical switching.

Self-assembled monolayers (SAMs) on metal surfaces have received much attention because of the importance of establishing how the surface properties can be altered by light and how the behavior of a SAM is affected by its structural rigidity [4,5].

A particularly important version of monolayer self-assembly occurs when a gold substrate contacts a suitable organosulfur compound [6,7]. This treatment results in a surface adsorbed monolayer possessing well-defined chemical and physical properties, that have been characterized by external reflection infrared spectroscopy (FTIR–RAS), contact angle goniometry, X-ray photoelectron spectroscopy (XPS), electrochemistry, ellipsometry, atomic force microscopy (AFM) and other techniques [6]. Such assemblies could provide a means for controlling both the chemical and physical properties of interfaces for a variety of heterogeneous phenomena including catalysis [8], corrosion [9], lubrication [10] and adhesion [11]. The ability to control interfacial properties has important implications from the point of view of both fundamental advances and technological advances.

We have previously reported the synthesis and self-assembly of a new squarylium dye-containing, alkanethiol unit with an amide group incorporated into the backbone [12]. A photochromic compound is characterized by its ability to undergo a reversible colour change on exposure to electromagnetic radiation in the UV/visible region. Although photochromic compounds have attracted significant attention because of their potential ability for sunlight-activated, self-coloured glasses as well as for optical memory media, they still await major commercial exploitation. One of the major reasons for this lack of industrial applications of photochromic materials, particularly organic photochromic compounds, is their poor durability.

Although the photochromism of the spiropyran system has been extensively studied [13,14], only a little work has been carried out on spironaphthoxazine dyes. While these two classes of compound are similar in many respects, the replacement of the benzopyran ring by a naphthoxazine ring results in a spironaphthoxazine having the advantage of greatly improved resistance to prolonged UV irradiation. This confers a greater commercial importance to the spironaphthoxazine compounds [15]. We have also reported the preparation and surface properties of a photochromic spiroxazine dye monolayer on gold [16].



colorless form colored photomerocyanine

X = CH ; spiropyran
X = N ; spiroxazine

The present paper deals with the surface properties and photoinduced refractive index changes in a photochromic spiroxazine-containing, alkanethiol monolayer on gold by use of SPR.

2. Experimental

2.1. Contact angle measurements

For the evaluation of surface wettability, the water contact angles of the nude gold, cystamine–gold and spiroxazine–cystamine–gold were measured at room temperature using a contact angle goniometer (Model G-I type, Erma Inc., Tokyo, Japan) [17]. A droplet of water was put on the air-side surface of a film at 25°C and, after 30 s, the contact angle was measured. More than 10 measurements were carried out for a single sample. The values obtained were averaged (Fig. 2).

2.2. AFM analysis

The topographic images of the sample surfaces were collected in the contact mode using a SPM-LS manufactured by Park Scientific instruments (PSI). The silicon nitride cantilevers had a nominal spring constant of about 0.05 N/m. The scanning parameters were adjusted to provide clear images, revealing the effects of SAMs on deposited gold surfaces.

2.3. Preparation of self-assembled monolayer

The gold surface was prepared by the electron-beam evaporation of 3 nm of nickel–chromium as an adhesion promoter, followed by 50 nm of Au, onto the glass slide. The stepwise, chemical assembly of the spiroxazine dye monolayer was performed by covalent linkage of the carboxyl unit of the spiroxazine dye to a cystamine-monolayer-modified gold surface.

The spiroxazine dye was prepared using previously described procedures [16]. A gold deposited glass slide was immersed in a 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 a 1×10^{-2} M, ethanolic solution of 1-ethyl-3-(3-(dimethylamino)propyl)-carbodiimide (EDC) and 5×10^{-4} M of spiroxazine dye for 12 h. The

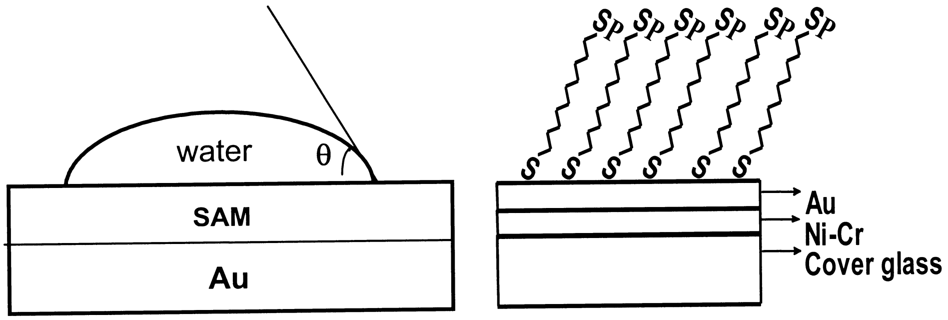


Fig. 2. Schematic representation of (a) a water droplet on a solid substrate and the contact angle, θ, (b) a multilayer system of SPR (sp: spiroxazine).

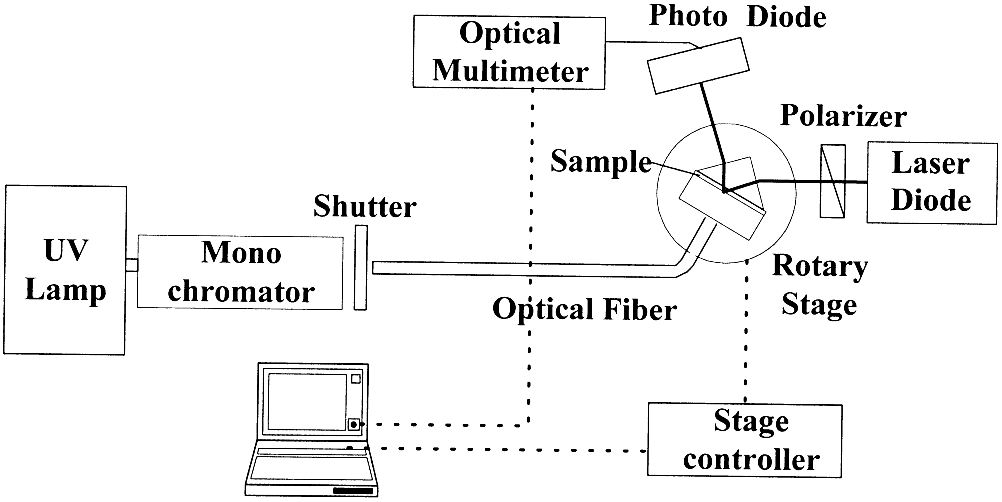


Fig. 3. Experimental set-up for measuring SPR angle shift of SAMs.

resulting monolayer was rinsed several times with deionized water and dried in N_2 gas.

2.4. Surface plasmon resonance(SPR) measurements

The experimental setup for measuring the SPR angle shift is shown in Fig 3. The slide glass with a spirooxazine-containing SAM formed on the gold surface and prism ($n_D = 1.515$, SIGMA, BK 7) is loaded on a computer-controlled rotating stage. Optical contact between the prism and slide glass was achieved by a refractive index matching fluid ($n_D = 1.515$–1.517, MERCK). The *p*-polarized laser diode, at 670 nm, was used as a polar beam. The reflected intensity, via a prism was measured with the photodiode detector (ANDO Electric Co. Ltd., AQ-1976) and by an optical multi-meter (ANDO Electric Co. Ltd., AQ-1135E). The angle was regulated by an automatic, motorized rotary stage controller with a resolution of 0.004°. A high-pressure mercury lamp (Ushio, SP3-250D) was used as the UV radiation source and was calibrated with a monochromator at 366 nm. In order to investigate the photochromic properties of SAMs with respect to refractive index changes, the UV light source was switched with a shutter and radiated on the SAMs layer.

2.5. Visible absorption spectra

A multi-channel photodiode detector (MCPD, Otsuka Electronics, Co, Japan) was used to obtain visible absorption spectra of SAMs on the gold surface. A light source, I_2 lamp, was projected and light collected using a Y-type optical fibre.

3. Results and discussion

We reported the synthesis and self-assembly of a spiroxazine dye that possessed an amide group incorporated into the backbone [16]. It is believed that the presence of the amide group in the chain provided orientational stability through intermolecular hydrogen bonding within the monolayer, thus enhancing the mechanical integrity of the assembly as a whole. A SAM was prepared from the stepwise chemical assembly of the spiroxazine dye shown in Fig. 4 and analyzed using contact angle measurements, UV–visible spectroscopy and surface plasmon resonance.

A chemical method of analysis has proven to be remarkably useful and sensitive in characterizing the surface functionality [18] and the structure [19] of SAMs. The ability to modify the end-group of the thiol adsorbates allowed us to vary the wetting

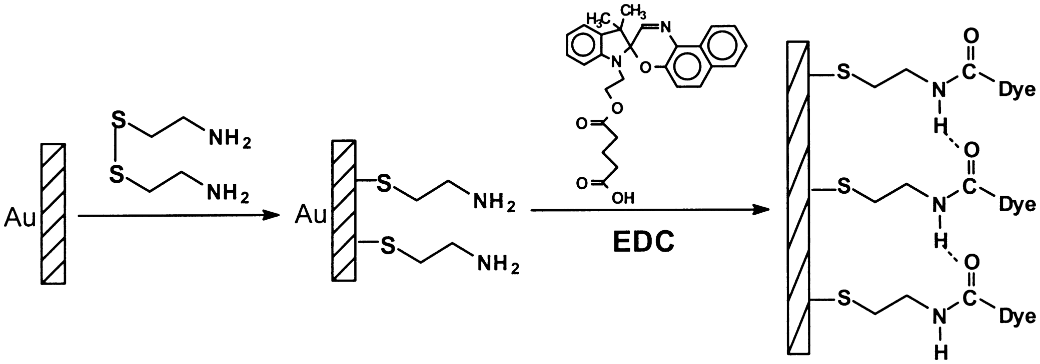


Fig. 4. Stepwise organization of a spiroxazine dye monolayer on Au layer.

Table 1
Water contact angle of surface-modified Au

Substrates	Contact angle (°)[a]
Nude gold	83±2
Au I	78±3
Au II	62±2
Au III	55±2

[a] Measured by contact angle goniometer.

properties of the monolayer extensively. The water-contact angles on nude gold, on cystamine–Au (Au I), on spiroxazine(closed form)–cystamine–Au (Au II), and on spiroxazine(open form)–cystamine–Au (Au III) are shown in Table 1.

The contact angle measurements show that surface-modified Au I, Au II and Au III are more hydrophilic than the nude gold surface. Au I had a contact angle of 78°, indicating that the amino group-terminated system is more polar than is the nude gold surface. The reduced contact angle of 62°, observed for Au II, can be rationalized by consideration of the structure of the spiroxazine SAM. The amide group is itself very polar. The presence of high densities of amide groups at the surface of SAM might have been expected to make the surface Au of SAM hydrophilic. The irradiation of the SAM on the gold surface, with UV light (366 nm), induced a large reduction in the contact angle as compared with that in Au II. The surface of Au III is even more hydrophilic than Au II. Unlike the closed form of spiroxazine, the open merocyanine form exhibits polar characteristics that can be explained by the three mesomeric forms, namely the quinonoidal form, the zwitterionic form and the resonance hybrid structure [16]. The change of contact angle between Au II and Au III is direct evidence of conversion from closed spiro form to photo-induced, open merocyanine form. The morphology of the SAM film was directly observed by AFM. Fig. 5 shows AFM images of (a) a nude gold surface, (b) a cystamine monolayer and (c) a spiroxazine modified monolayer linked to cystamine.

Surface roughness is a relative concept. In the engineering industry the most universally recognized roughness parameter is the arithmetic mean value for line profiles, R_a. Other, often used, amplitude parameters are the average between the five highest peaks and the five lowest valleys; Rz(ISO), the peak-to-valley value, R_t; and the standard deviation or root-mean-square (rms) roughness, R_q, of the surface hights relative to the least-squares fit of the profile. R_a and R_q are both averages of the height variations. R_q is more sensitive to large height deviations than R_a is. R_q has a direct relationship to the light-scattering properties of surfaces and has, therefore, been accepted as the de facto standard as a roughness parameter in the optics community.

The mean value of the heights from the cross-sectional analysis of nude gold, the surface roughness, R_q, is about 1.04 nm (Fig. 5a). The image of cystamine deposited surface on the gold surface shows a similar shape to the surface of nude gold. The surface roughness, R_q, is 1.25 nm (Fig 5b). The SAM film of the spiroxazine–cystamine–gold

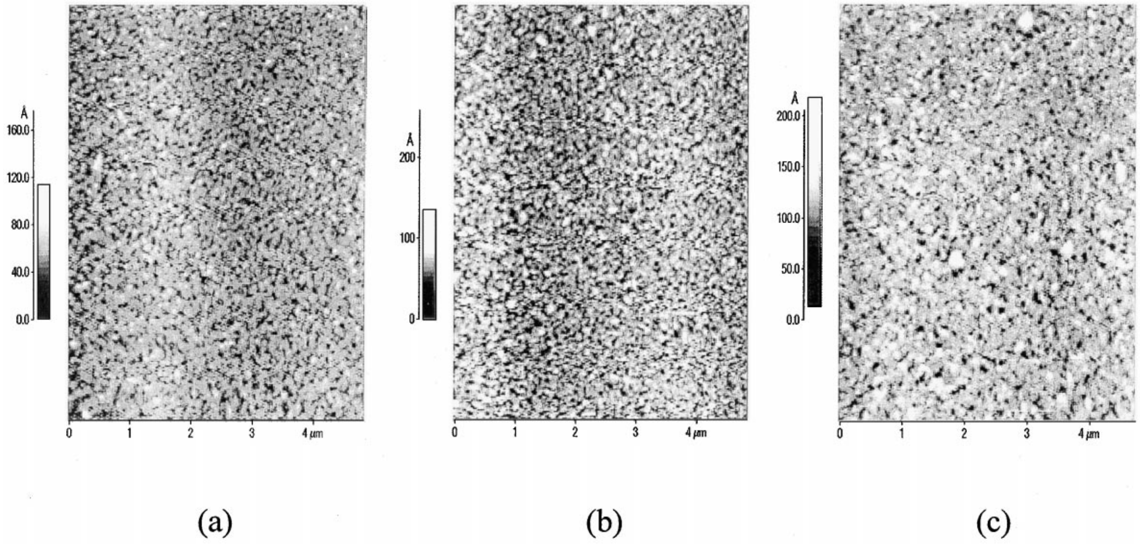


Fig. 5. Atomic force microscope image of the film surface (a) bare gold, (b) cystamine–gold and (c) spiroxazine–cystamine–gold.

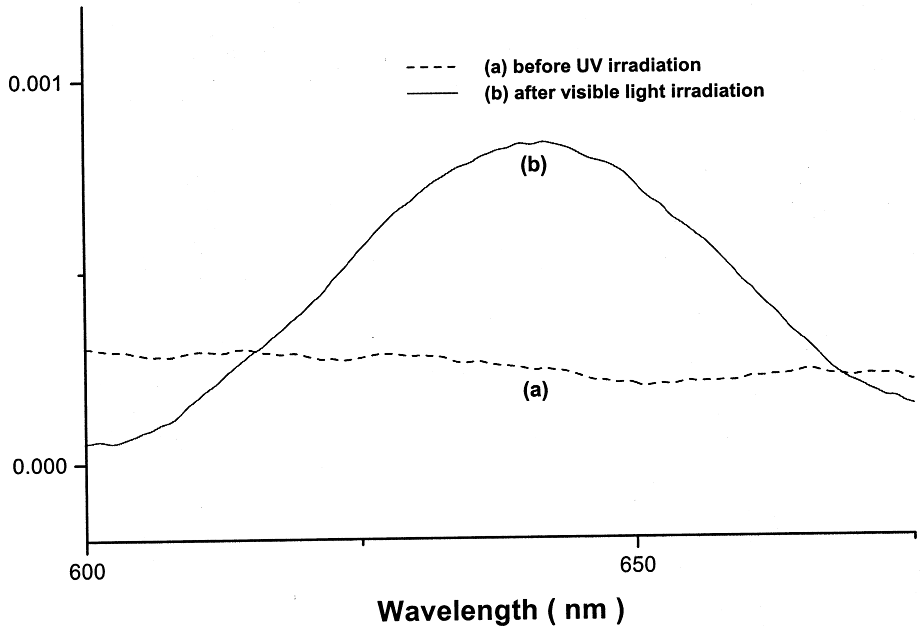


Fig. 6. Absorption spectra of SAM.

is composed of much greater grain size. Its surface roughness is 1.59 nm. This increased surface roughness arises from the stepwise chemical assembly.

In liquid or solid solution, the spiroxazine turns blue upon irradiation with UV light and rapidly fades back to being colorless when the activating radiation is removed. Only UV-A (315–380 nm) is required for activation. Fig. 6 exhibits a visible absorption spectrum of a SAM film of the spiroxazine dye. Upon irradiation with 366 nm light, a new absorption peak appears at around 640 nm; the original spectral pattern is reversibly recovered within 60 min. The new band is ascribable to the generation of the open merocyanine form from the closed spiroxazine form.

SPR is a resonance phenomenon in which surface plasmon waves are excited at a metal/dielectric interface, as illustrated in a classical configuration in Fig. 1. In the SPR method, the resonance angle is very sensitive to variations of the refractive index of the medium outside the metal film. Optical excitation and detection of the SPR phenomenon can be used to measure the refractive index of either bulk chemical samples or thin film chemical transducing layers. At the surface plasmon resonance coupling angle, θ, the reflected intensity is attenuated as a result of the incident optical energy being transferred to the SPR charge density curves. The refractive index of the dielectric layer can be calculated from the experimentally measured SPR coupling angle, θ. Fig. 7 shows the SPR curves for the SAM with the photochromic spiroxazine dye both before and after exposure to UV (366 nm) irradiation. Fig. 7 shows the changes in resonance angles induced by UV irradiation by the formation of the photoinduced merocyanine form.

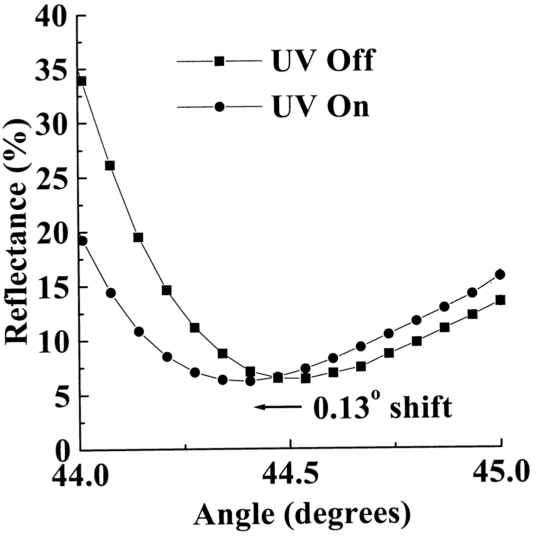


Fig. 7. Resonance angle shift of SAMs upon UV irradiation.

The resonance angles, before and after irradiation, were 44.54 and 44.41°, respectively.

Surface plasmon generation occurs only if the wavevector matching condition is satisfied by the following equation [20].

$$n_{\mathrm{p}} \sin \Delta\theta = \sqrt{\frac{n_{\mathrm{m}}^2 \Delta n_{\mathrm{s}}^2}{n_{\mathrm{m}}^2 + \Delta n_{\mathrm{s}}^2}}$$

Here, $n_{\mathrm{p}}, n_{\mathrm{s}}, n_{\mathrm{m}}$ are the refractive index of prism, sample (SAM film) and metal (Au), respectively. The above equation shows that the refractive index change, Δn, of SAMs relates directly to the resonance angle shift, $\Delta\theta$, to the given $n_{\mathrm{p}}, n_{\mathrm{m}}, \Delta\theta$, the refractive index change can be calculated easily using the equation. From the resonance angle shift change, $\Delta\theta = 0.13°$, $n_{\mathrm{m}} = 0.142$, and $n_{\mathrm{p}} = 1.514$, refractive index change ($\Delta n = 0.0034$) before and after UV irradiation was obtained.

These results strongly suggest that the present SPR system, based on a spiroxazine SAM film, could be useful in molecular photonics for optical switching.

Acknowledgements

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