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Surface plasmon resonance study on the interaction of a dithiosquarylium dye with metal ions

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Abstract

The detection of some metal ions has been investigated using an optical sensor based on surface plasmon resonance (SPR). A multilayer sensing chip was prepared with a dithiosquarylium (DTSQ) dye sensing layer coating on a gold layer. Using the DTSQ dye as a metal ion sensing molecule, a highly selective response for Ag^+ was observed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Surface plasmon resonance (SPR); dithiosquarylium (DTSQ) dye; Metal ion sensor; Resonance angle

1. Introduction

Surface plasmon resonance (SPR) is one of the promising optical techniques for chemical sensing, and SPR configuration systems such as immunoassay [1], liquid [2], gas [3] and thin films [4] have been reported.

A surface plasmon is a surface charge-density wave at a metal surface. It is well known that surface plasmons can be excited by the attenuated-total-reflectance (ATR) method reported by Kretschmann [5]. Since the resonance angle is very sensitive to variations in the refractive index of the medium just outside the metal thin film, the refractive index of a film, e.g. multilayer Langmuir–Blodgett film [6] or polymeric film [7], can be 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 a solution depends solely on analyte concentration. This can be performed by employing selective chemical sensing layers (e.g. selective membrane, chromoionophore, and specific binding layer). A chemical sensing layer consists of a thin film having optical properties that vary with concentration of the analyte to be sensed.

Squarylium dyes are 1,3-disubstituted compounds synthesized from squaric acid and two equivalents of various types of electron-donating carbocycles or heterocycles such as azulene [8], pyrroles [9] or heterocyclic methylene bases [10].

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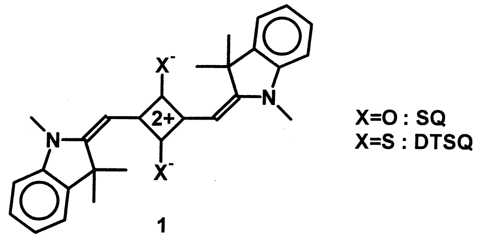
This class of dyes has attracted much attention because of potential applications in xerographic organic photoreceptors [11,12], optical recording media [13] and organic solar cells [14]. They possess properties such as photoconductivity and a sharp and intense absorption in the visible or near infrared region [15].

We have previously reported the synthesis [16], electroluminescence [17] and eletrophotographic properties [16] of dithiosquarylium (DTSQ) dyes. Also reported was the metal ion recognition of squarylium (SQ) and DTSQ dyes **1** by film optode [18]. In this paper we report the development of an Ag^+ ion sensor and demonstrate that SPR is capable of sensing Ag^+ ions using a DTSQ dye.



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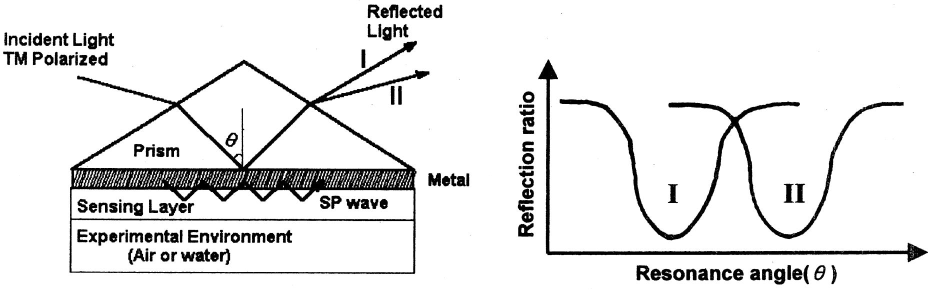
2. Principle of operation

Surface plasmon waves (SPWs) are excited at the interface between a thin, highly reflecting metal layer (e.g. silver or gold) and a 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 normal to the surface. Since surface plasmons only have an electric field component, which is 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 is the 'sensing' component and can interact optically with compounds close to or at the surface. Changes in the optical properties of this region will influence the SPR angle, and accounts for the use of SPR for sensing purposes.

3. Experimental

The SPR system used in this study is based on the traditional Kretschmann prism method [5]. Gold film (500 Å thick) was deposited on a glass slide by electron-beam evaporation, using a 30 Å nickel-chrom under layer for adhesion. The polymeric sensing membrane coated sensor chip and prism ($n = 1.515$, Sigma, BK7) were loaded on



(a) (b)

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

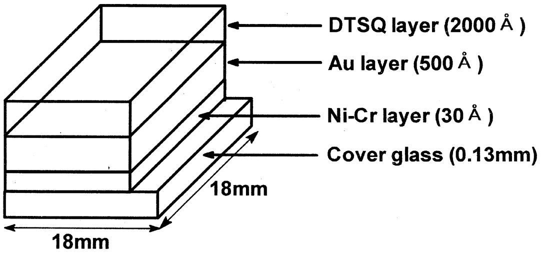


Fig. 2. Multilayer design of the SPR sensing element.

the sample solution cell using a micrometer. Optical contact between the prism and this sensor chip is achieved by a refractive index matching fluid (*nD* = 1.151–1.517, Merck). The polarized incident light from a laser diode (4.5 mW, 670 nm) was reflected and detected by a photo diode detector (Ando Electric Co. Ltd., AQ-1976) with a multimeter (Ando Electric Co. Ltd., AQ-1135E). The intensity of reflected light was detected and used to change the incident angle of polarized light. This angle was regulated by an automatic-motorized rotary stage controller with a resolution of 0.004°.

The incident angle that shows the smallest optical reflectance was varied with the change of Au surface dielectric constant that arises from the interaction between the DTSQ dye in a polymeric sensing membrane and a metal ion. The casting solution used to prepare the polymeric sensing membrane was a high molecular weight PVC-PVAc-PVA copolymer (Aldrich Chemical Company Inc., M.W. = 27,000, 14.82 w/w%). DOP (dioctyl phthalate, Aldrich Chemical Company Inc., 64.66 w/w%) as a plasticizer, lipophilic anionic site [potassium tetrakis(4-chlorophenylborate], Fluka, 6.26 w/w%), and DTSQ dye (14.26 w/w%) in THF (Junsei Chemical Co. Ltd.). Due to their higher stability and liphophilicity, borate salts were used for the cation selective membrane. This casting solution was spin-coated on the well-cleaned surface of the cover glass (membrane thickness = 0.2 μm). Fig. 2 shows the principal construction of the sensing chip. The concentrations of metal ions [$M^{n+}(NO_3)_n$, $M^{n+} = Cu^{2+}$, Ag^+, K^+, Na^+, Zn^{2+}] ranged from 1×10^{-4} M to 1×10^{-12} M (in Tris–HCl buffer, pH = 7.0, 0.1 M) and were prepared to measure the intensities of reflected light and their resonance angle shifts. All sample solutions were pumped into the sample cell starting at low concentrations, and the sample cell was washed with a buffer solution before measuring a different sample. The experimental set-up is shown in Fig. 3.

4. Results and discussion

The development of sensors providing an optical transduction of the chemical recognition process

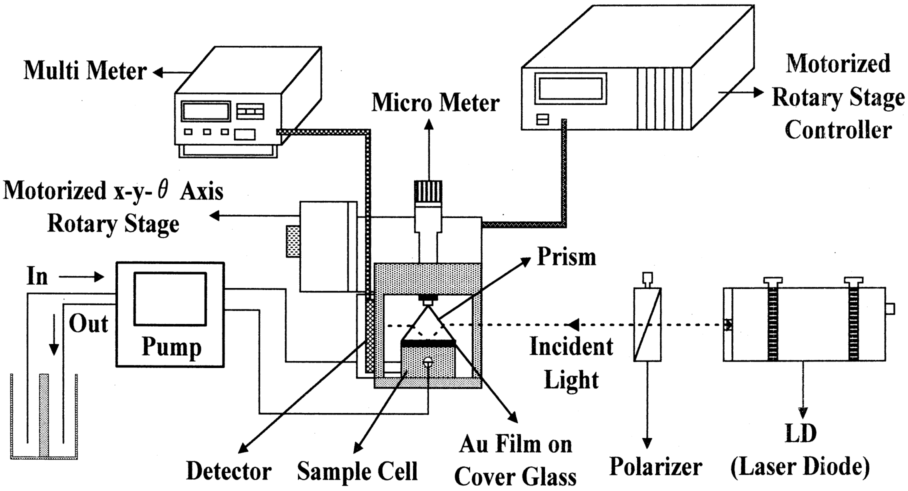


Fig. 3. Diagram of a SPR-based chemical sensor system.

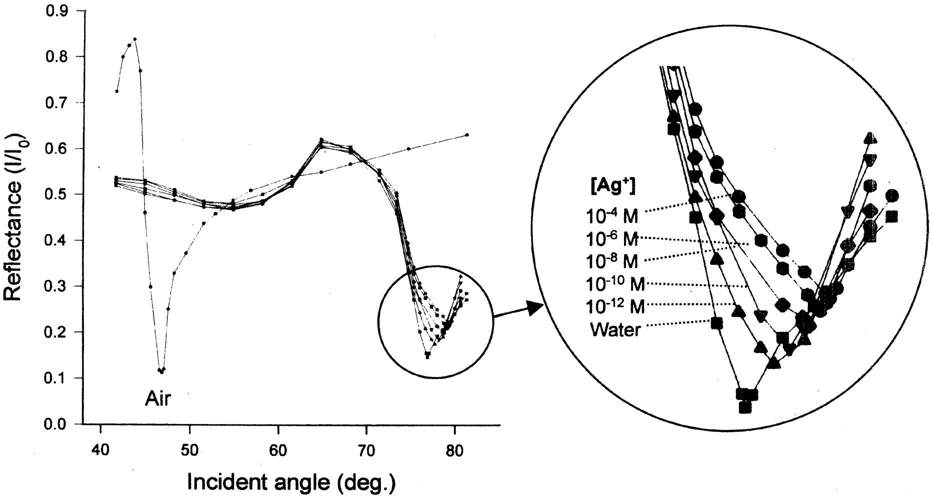


Fig. 4. The effects of coating a gold film with sensing membrane containing DTSQ on SPR waves.

has become a highly relevant and rapidly expanding area in analytical chemistry [19]. In this regard, the design of fluorescent or chromogenic chemosensors for the selective detection of low concentrations of ions, is an active area of research. Highly selective ion sensing film optodes for the determination of metal ions have been prepared with plasticized PVC–PVAc–PVA membranes containing a SQ or DTSQ dye [18]. The results indicated that SQ and DTSQ showed a striking selectivity for Cu^{2+} or Ag^{+} complexation.

Here we report the development and application of ion sensing SPR which can easily determine various ions such as Ag^{+}, Cu^{2+}, K^{+}, Na^{+} and Zn^{2+}, all of which are biologically and environmentally important species. The DTSQ dye employed affords the prospect of rapid, reversible and sensitive response to Ag^{+} at room temperature, which are prerequisites for successful application of SPR.

In the surface plasmon method, the resonance angle is very sensitive to variations in the refractive index of the medium outside the metal film. When the medium outside the gold layer changed from air to pure water, the resonance angle changed from 46.92 to 76.88, as shown in Fig. 4. Fig. 4 shows the changes in resonance angles induced by added Ag^{+}. It is clear that increased Ag^{+} concentration afforded an increase in the resonance angles. When solutions of different metal ion concentrations were used, shifts in reflectivity were obtained. The shift in incident angle increased linearly with the concentration of metal ions, as shown in Fig. 5. Fig. 5 also shows that the addition of metal ions such as Cu^{2+}, Zn^{2+}, Na^{+} and K^{+} up

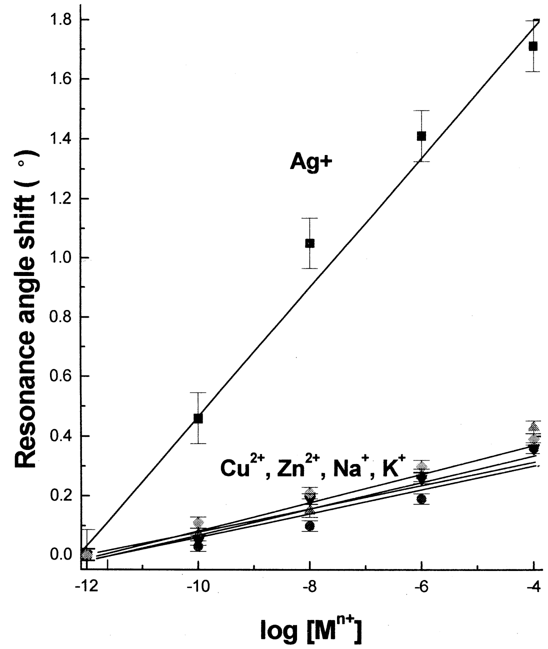


Fig. 5. Calibration plots for metal ions obtained with SPR.

to 1×10^{-4} M did not have a significant effect on the resonance angle. The slopes of the straight lines, which correspond to sensitivity, indicated that the sensitivity for Ag^{+} ion was relative high whereas the other metal ions were not sensitive.

Owing to detection at trace levels and a specific response to Ag^{+} in SPR, DTSQ dye appears to be suitable for practical SPR sensor application.

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