Detection of Dye Molecules Adsorbed in a Mesoporous Layer by Surface Plasmon Resonance Spectroscopy and its Comparison with Simulation Results

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Abstract. We report in this paper, the utilization of Surface Plasmon Resonance (SPR) spectroscopy to distinct the adsorption type of dye molecules into an Aluminium-doped Zinc Oxide (AZO) mesoporous layer. This was performed in a Kretschmann configuration by measuring the SPR spectra at various incident angles. The SPR spectral dips were then compared with the simulation results calculated on the basis of the transfer-matrix method. There is an agreement between the simulation results and experimental results, which confirm two different kinds of dye adsorption. The first type is pure dye adsorption into the mesoporous layer, while the second type is dye adsorption accompanied by dye deposition on the mesoporous surface.

1. Introduction

Some optical devices and sensors, such as dye-sensitized solar cells (DSSC), optical gas sensors, biochemical sensors, are built by a mesoporous layer as its active layer. [1-7] The thickness of the layer may be in a few micrometers, but it is also often in a few tens of nanometer. Small dye molecules are often impregnated into the mesoporous layer as active molecules or sensing molecules. While the dye deposition on the surface can be confirmed by some microscopy techniques, such as scanning electron microscopy (SEM) or atomic force microscopy (AFM), the dye adsorption inside the mesoporous layer is not easy to be confirmed. For that purpose, Surface Plasmon Resonance (SPR) spectroscopy may provide an alternative way due to large penetration depth of surface plasmon wave on the metal/dielectric interface.

SPR is an evanescent wave generated by resonance of an incident p-polarized light wave resonances with plasmon oscillation occurred at the interface between thin metal film ($\varepsilon_m$) and dielectric ($\varepsilon_d$). SPR can be generated by various means by using a prism coupler or a grating coupler, waveguide, structure and metal nanoparticle structure. In case of SPR generation by using a prism coupler, the resonance condition is given by

$$\frac{\alpha}{c} \sqrt{\varepsilon_p} \sin \theta_o = \frac{\alpha}{c} \sqrt{\varepsilon_m \varepsilon_d}$$

(1)

where $\omega$ is the angular frequency, $c$ is the speed of light, $\varepsilon_p$ is the dielectric permittivity of the prism, $\theta_o$ is the incident angle of the p-polarized incident light, $\varepsilon_m$ is the dielectric permittivity of the metal layer and $\varepsilon_d$ is the dielectric permittivity of the dielectric layer. While in many cases we found the dielectric layer is not a light absorbing material, in the present work we consider it is a light absorber.
due to the dye molecules in the mesoporous layer. In such case, the dielectric layer becomes an absorbing layer. The eq. (1) is still applicable, but the dielectric permittivity \( \varepsilon_d \) is now a complex number. In this paper, we report our evaluation on the possibility of SPR spectroscopy for detecting the adsorption of dye molecules inside a mesoporous layer.

2. Methodology

2.1. Experimental

![Illustration of the a) adsorbed type, and b) adsorbed and surface deposited type of dye in AZO mesoporous layer, respectively.](image)

Figure 1. Illustration of the a) adsorbed type, and b) adsorbed and surface deposited type of dye in AZO mesoporous layer, respectively.

In this work, we consider two types of dye adsorption cases, namely the adsorbed type (type I) and the adsorbed and surface deposited type (type II), as illustrated in Figure 1. The SPR generation in those structures was carried out by using a prism coupler in the Kretschmann configuration. In such configuration, in order to have resonance wavelength at visible region, the dielectric permittivity of the substrate and the dielectric layer should be smaller than the permittivity of the prism coupler. Therefore, in this work, we controlled the AZO layer to be thin enough so that the thickness was quite smaller compared to the penetration depth of the SPR wave. In such case, the permittivity of the AZO layer was smaller than the prism coupler permittivity (\( \varepsilon_p = 2.25 \)), although the bulk AZO permittivity is around 3.24.

2.1.1. Samples

Au thin layer with the thickness of 50 nm was deposited onto a glass substrate by sputtering method. The AZO precursor solution was synthesized by a method reported elsewhere by dissolving 0.25 M zinc acetate dehydrate (\( \text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} \)) in 2-methoxyethanol with diethanolamine (DEA) as the stabilizing agent and AlCl3 as the Al dopant. [8-9] The solution was stirred for 24 hours. This AZO precursor solution was then spin coated onto an Au thin layer, which was subsequently subjected to heat treatment up to 500°C. The thicknesses of these AZO layers were about a few tens nanometer, which was supposed to be much smaller than the penetration depth of the SPR wave. These AZO layers were then immersed in dye N719 solution in 0.25 hour and an hour.

![The experimental set-up of SPR spectroscopy used in this work.](image)

Figure 2. The experimental set-up of SPR spectroscopy used in this work.
2.1.2. Experimental set-up
The measurement of SPR spectrum was performed by using the \textit{p}-polarized polychromatic light from a tungsten lamp in Kretschmann configuration at several incident angles. The reflected beam from the SPR element was captured by a light guiding and then delivered to the CCD based spectrophotometer, as indicated in Figure 2.

2.2. Simulation
The SPR spectra were simulated by using a simple calculation based on the transfer-matrix method for multilayer structures at oblique incidence. The relationship between the electric field at the \textit{i}-th layer and the nearest adjacent \((i+1)-th\) layer is given by \([10,11]\)

\[
\begin{bmatrix}
E_i^{x}\nn_i
\end{bmatrix}_{i+1} = \frac{1}{\Gamma} \begin{bmatrix}
r_{i}e^{i\phi_{i}}
\end{bmatrix} E_{n+1}^{x} \tag{2}
\]

The total reflection coefficient is then given by

\[
\Gamma = \frac{r_{i}e^{i\phi_{i}}E_{n+1}}{E_{i}} \tag{3}
\]

and the reflectance \(R\) is given by

\[
R = |r_{i}|^2 = \prod_{i=1}^{N-1} |f_{i}|
\tag{4}
\]

Figure 3. Electric field and other notations in multilayer structure model used in the simulation.

3. Results and discussion
3.1. SPR spectra of the Au thin layer
As the first step, the SPR spectra of an Au layer with a thickness of 50 nm in the prism/Au/air configuration was characterized and then compared with simulation based on the transfer matrix method. In the simulation, the dielectric permittivity was set to be close as in the experiment, i.e. \(\varepsilon_{\text{prism}}=2.25\), and \(\varepsilon_{\text{air}}=1\), while \(\varepsilon_{\text{Au}}\) was calculated based on the Drude-Lorentz model. Figure 4 shows that the spectra obtained from the experiment are almost similar as obtained from the simulation. At
the same incident angle, the SPR dip, which is indicated by the reflectance dip, appears at almost the same wavelength in both experimental and simulation spectra. The dip is blue shifted with increasing incident angle.

3.2. SPR spectra of the Au/AZO layer

Figure 5.(a) shows the SPR spectra of the Au/AZO layer in the prism/glass/Au/AZO/air configuration, which seems different from the Au layer spectra in Figure 4.(a). The dips are shifted to longer wavelength for the same incident angle, which indicates larger permittivity due to the presence of AZO thin layer. However, the AZO layer is quite thin so that the resonance wavelengths are still in the visible region. Figure 5.(a) shows the simulation results with the parameters: $\varepsilon_{AZO} = 3.2400$ and the AZO thickness is about 20 nm. In this simulation, we disregarded the wavelength dependence of the dielectric permittivity of the AZO layer. The dielectric permittivity was considered to be almost constant in the wavelength region considered here. We can see clearly that the dip wavelengths are almost similar in the experimental and the simulation spectra.

![Figure 4](image4.png)

Figure 4. The SPR spectra of an Au layer with a thickness of 50 nm in the prism/glass/Au/air configuration obtained from a) experiment and b) simulation.

![Figure 5](image5.png)

Figure 5. The reflectance of the prism/glass/Au/AZO/air configuration obtained from a) experiment and b) simulation.

3.3. SPR spectra of the Au/AZO+dye layer

After the immersion in N719 dye solution in 0.25-hour, the sample color changed into transparent red color, indicating a dielectric permittivity with a complex number consisting of the real and imaginary values. It is, however, not easy to determine it experimentally. We suppose that in this situation the sample is the type I in Figure 1, which is the porous adsorbed type. Figure 6.(a) shows
the SPR spectra where the dip is further shifted to a longer wavelength and the dip becomes shallower. This is due to the increase of both real and complex parts of the total permittivity caused by the dye infiltration into the AZO mesoporous layer. The SPR spectra from the simulation seem similar to the experimental results, where in this simulation we used the parameters: \( \varepsilon_{\text{AZO}+\text{dye}} = 3.9998 + 0.08 \) i and the AZO+dye layer thickness is 20 nm. Here, we considered again that the dielectric permittivity is almost constant in the evaluated wavelength region. The imaginary value indicates the absorption effect from the dye.

3.4. SPR spectra of the Au/AZO+dye/dye layer

Figure 6. The SPR spectra of Au/AZO+dye layer obtained from a) experiment, and b) simulation.

Figure 7. The reflectance of the Au/AZO+dye/dye layers obtained from a) experiment and b) simulation.

Immersion in into the dye solution in a longer time, that is, in an hour, seems to produce the SPR spectral dips appeared in the shorter wavelength region. The dips now appear at around 600 nm for incident angels around 42°-44°. This shifting seems unusual. However, in this case, the sample color visually become darker red color, supposing the dye deposition on the surface of the AZO layer, as illustrated as the type II in Figure 1. The simulation results nevertheless support that layer formation as shown in Figure 7.(b). The simulation shows the appearance of SPR dip around 600 nm obtained by using dielectric permittivity parameters: \( \varepsilon_{\text{AZO}+\text{dye}} = 3.9998 + 0.08 \) i with the AZO+dye thickness is 20 nm and \( \varepsilon_{\text{dye}} = 6.2496 + 0.1 \) with the surface deposited dye layer thickness is 30 nm.

Finally, the agreement between the experimental and the simulation results are shown in Figure 8, which is indicated by the points scatter around the theoretical curve lines in the dispersion curve.
The theoretical dispersion curve lines calculated from the eq. (1) are also shown for dielectric constant $\varepsilon_d = 1$ (for prism/Au/air) and for effective dielectric permittivity $\varepsilon_d = 1.25$ (for prism/Au/AZO) as a comparison. The effective dielectric permittivity here is much smaller than the dielectric permittivity of AZO bulk, which indicates that the AZO layer is extremely thin so that the upper portion of SPR wave widely overlaps with the air, as illustrated in Fig. 1.

Figure 8. The dispersion curves obtained from a) the experiment and b) simulation results. The theoretical dispersion curve lines calculated from the eq. (1) for $\varepsilon_d = 1$ and 1.25 are also shown for comparison.

4. Conclusion
The present work shows that this SPR spectroscopy can be used effectively as a non-destructive tool for identifying the adsorption of dye molecules inside a mesoporous layer. A combined method of experiment and simulation can distinguish well the two different types of dye adsorption in the mesoporous structure.

5. References
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