Chapter 109
Surface Plasmon Resonance

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Biosensor · Fluorescence enhancement

109.1 Principle

"Surface plasmon polariton (SPP)" is collective oscillation of electrons at a metal–
dielectric interface, which holds a specific longitudinal wave vector, k_{sp}, lying along
with interface as a function of frequency.

$$k_{sp}(\omega) = \frac{\omega}{c} \sqrt{\frac{\varepsilon_m(\omega)\varepsilon_d(\omega)}{\varepsilon_m(\omega) + \varepsilon_d(\omega)}}, \tag{109.1}$$

where ε_m ($=\varepsilon'_m + i\varepsilon''_m$) and ε_d ($=\varepsilon'_d + i\varepsilon''_d$) are complex dielectric functions of metal
and dielectic materials. ω and C are the angular frequency and the light velocity in
vacuum. This equation is called as SPP dispersion equation. When a laser light is
irradiated to a metal–dielectric interface with an incident angle θ, the photon wave
vector of the incident light projected to the metal–dielectric interface, k_{ph}^x, is
described as:

$$k_{ph}^x(\omega) = \frac{\omega}{c} \sqrt{\varepsilon_d(\omega)} \cdot \sin\theta, \tag{109.2}$$

 when $k_{ph}^x = k_{sp}$, a resonance coupling between photons and SPP can be maintained.
This phenomenon is called as "surface plasmon resonance (SPR)." In general,
Kretschmann-based prism couplers are utilized to achieve the above condition
(Fig. 109.1), where evanescent waves at the interface under the total internal
reflection couple with SPP on metal thin films (typically 50 nm-thick gold or

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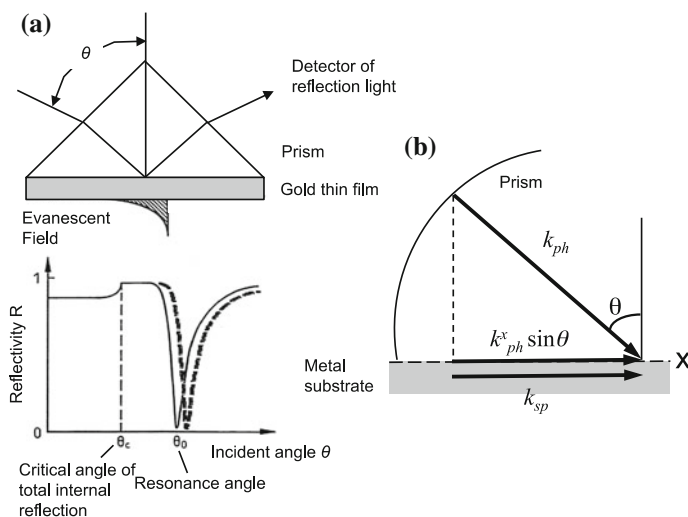e-mail: tamada@ms.ifoc.kyushu-u.ac.jp

(a)

(b)

Fig. 109.1 a Kretschmann-based prism coupler for SPR measurement (*top*) and the typical angular scan data to determine SPR resonance angle (θ_0) (*bottom*). The resonance angle shifts to larger angles when molecules adsorb on gold surface. **b** Schematics of wave vector matching for resonance coupling of photon and SPP at a metal–dielectric interface. At θ_0, the photon wave vector projected to the interface (x–y plane) matches the SPP wave vector, i.e., $k^x_{ph} = k_{sp}$

silver). The resonance condition can be tuned by the incident angle θ. The SPR coupling can be detected experimentally by monitoring the reflection light intensity [1, 2]. At the resonance angle (θ_0), the reflected light intensity becomes minimum as shown in Fig. 109.1a.

Surface-sensitive sensing measurement with SPR is performed by use of the metal surface at the opposite side of prism (open surface). The SPR wave excited at a metal/dielectric interface propagates in the x–y plane, while electric field penetrates into the dielectric medium and decays exponentially. The penetration depth in the dielectric medium is typically a few hundred nanometers, and the refractive index (dielectric functions) at this depth region determines the excitation condition of SPP (see Eq. 109.1). Thus, adsorption of small molecules having different refractive index from original medium (e.g., protein adsorption in water) can be detected sensitively by the resonance angle shift.

This type of SPR, excited on metal thin film, is called as "propagation" mode of SPR, in contrast to metal nanoparticle-based SPR ("localized" mode) [3]. Both SPR are widely used for analytical tools, because of their surface sensitive property, based on light confinement and enhancement effects. Those are used not only for refractive index detections but also for fluorescence or vibration signal enhancement (e.g., plasmon-enhanced fluorescence [4], surface enhanced Raman spectroscopy (SERS) [5]). The fields related to SPR are really wide, but this chapter focuses on a guidance of basic technique based on "propagation" mode of SPR with a prism coupler. For a grating-based SPR or a long-range SPR with Otto configurations, please refer the following references [6, 7].

109.2   Features

- Surface sensitive detection method with metal thin film.
- Typically used for detection of refractive index change, which leads to label-free, real-time biosensor application.
- SPR is used to enhance fluorescence or molecular vibration signals as well.

109.3   Instrumentation

One example of experimental setup for SPR measurement is schematically shown in Fig. 109.2. In a Kretschmann geometry system, a triangular prism (LaSFN9 glass) is index-matched to LaSFN9 substrates with the gold (or silver) films via immersion oil. A *p*-polarized He–Ne laser beam ($\lambda = 632.8$ nm, 5 mW) is mechanically chopped in conjugation with a lock-in amplifier before entering the prism. The intensity of the laser beam reflected at the prism–gold interface is monitored by a photodiode detector. The change of reflectivity as a function of the incident angle is recorded as "angular scan" data on a θ–2θ rotation stage, while kinetics scan data are recorded as a function of time at a fixed incident angle. The resolution of measured resonance angle is 0.01°–0.001°.

Before the measurement of samples, the angular scan of the bare gold film was taken in order to determine the exact gold film thickness and the complex dielectric constant, ε_m ($= \varepsilon'_m + i\varepsilon''_m$), by curve fitting with Fresnel's equations. Next, probe molecules are immobilized on gold (in many cases, by injection of thiolated probe molecules into the fluid cell), and then target molecules are injected. At each step, adsorption reaction is real-time monitored by the change in reflectivity via the
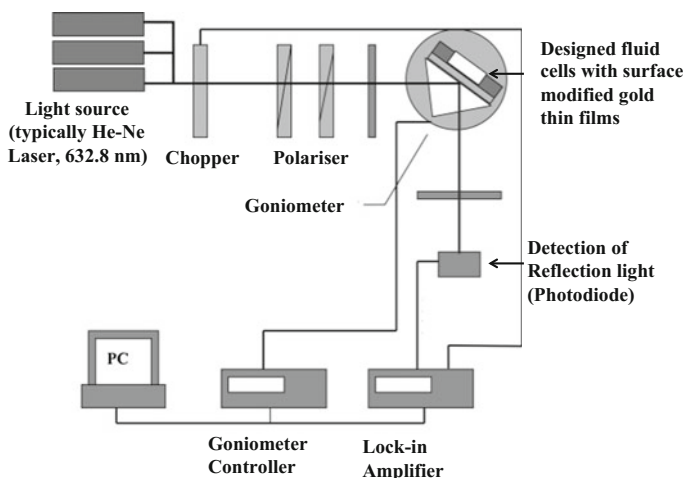

Fig. 109.2 Typical experimental setup for SPR measurement

kinetics scan. After the reflectivity reaches a constant value, the surface is rinsed by a pure solvent, and the thickness or refractive index of the formed layer is determined by the angular scan.

To conduct plasmon-enhanced fluorescence measurement, fluorescence-labeled target molecules or fluorescence marker molecules are injected into the fluid cell. The fluorescence intensity is monitored from the back window together with the reflectivity from the prism side.

109.4 Applications

109.4.1 Detection of Photoisomerization Reaction of Azobenzene SAM

One example of high-sensitive detection of molecular reaction is a monitoring of photoisomerization of azobenzene [8]. In Fig. 109.3, the photoswitching reaction is monitored in situ through the change of reflectivity with SPR setup. In this study,
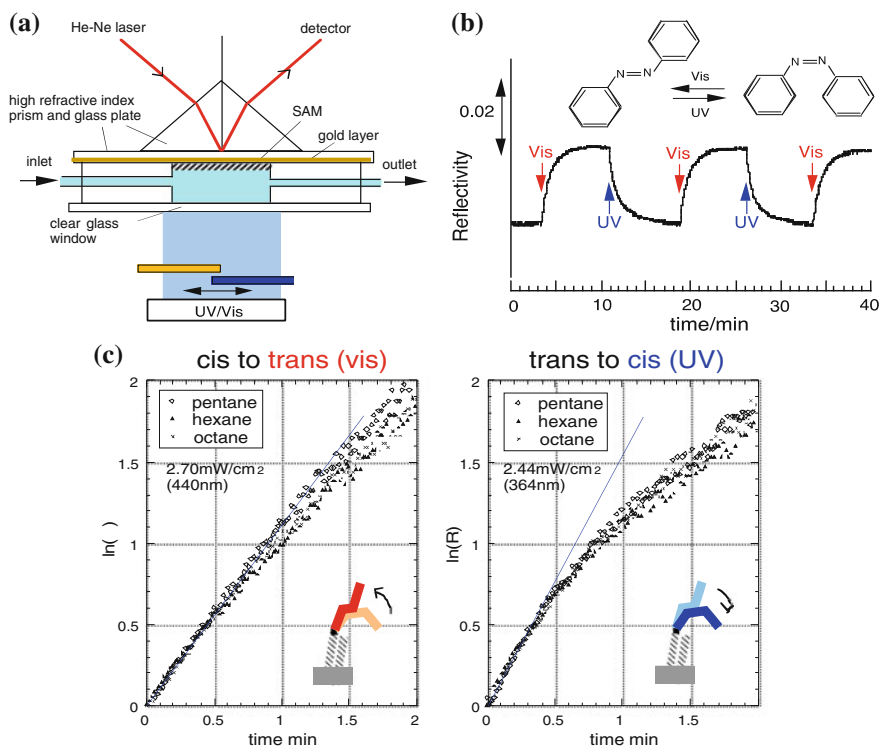

Fig. 109.3 **a** SPR set-up, **b** real-time monitoring of photoisomerization of azobenzene SAM and **c** the data analysis of reaction kinetics based of the first-order plots

self-assembled monolayers (SAMs) composed of azobenzene disulfides were utilized. From the data analysis of the trans-to-cis and cis-to-trans photoisomerization kinetics, a steric hindrance effect on the photoreaction process is clearly demonstrated.

109.4.2   Detection of DNA Hybridization Reaction

Another example of high-sensitive detection of molecular reaction is a hybridization of DNA molecules on surface (Fig. 109.4) [9]. Here probe DNA is immobilized by surface coupling reactions. In this study, the target DNA is only 20 or 50 mer, which is close to the detection limit of the conventional SPR method. To enhance the resonance angle shift, gold nanoparticles are utilized as a maker. The hybridization of target DNA-modified gold nanoparticles on the probe DNA realized ∼10 times enhanced resonance angle shift (reflectivity in kinetics mode) compared with the DNA molecules. The enhanced SPR signal by immobilization of gold nanoparticles is well reproduced by the simulation based on the Maxwell-Garnett theory and Fresnel's equation. This technique leads to the fabrication of high-resolution DNA microarrays in combination with the SPR microscope [10].
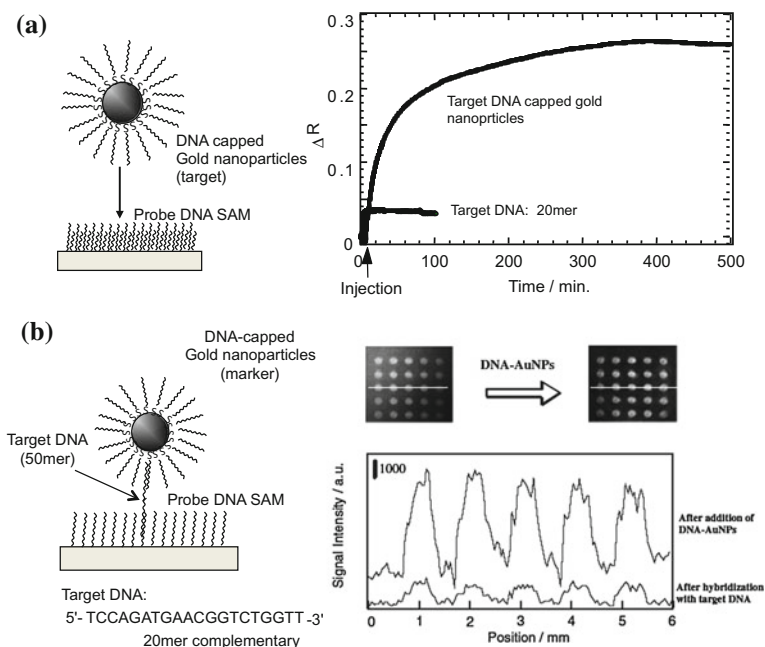

Fig. 109.4 a Change of refractivity by hybridization of DNA molecules and DNA-capped gold nanoparticles. **b** Sandwich assay by use of DNA-capped nanoparticle marker

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