Mesoporous silica thin films as a spatially extended probe of interfacial electric fields for amplified signal transduction in surface plasmon resonance spectroscopy†

Taewook Kang, Seogil Oh, Surin Hong, Jungwoo Moon and Jongheop Yi*

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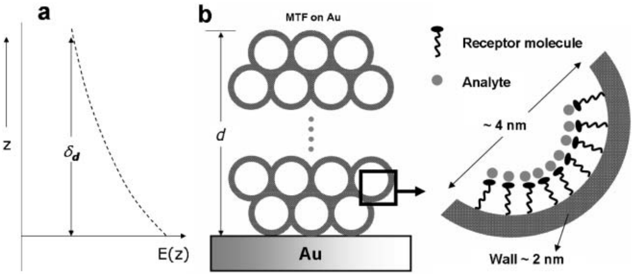
A new simpler concept about the signal amplification of surface plasmon resonance (SPR) that is based on the utilization of mesoporous silica thin films is demonstrated. As compared to monolayer based coatings, mesoporous silica thin films of ∼200 nm extend the interaction arena away from the metal, thus permitting the integration of the change in optical contrast at different distances from the sensor surface.

In the present communication, we describe a new simplified strategy for the signal amplification of surface plasmon resonance (SPR), based on the integration of the change in optical contrast by mesoporous silica thin films and demonstrate the extent of increased SPR sensitivity in a quantitative manner.

SPR is one of the most popular transduction principles in bio- and chemical sensors due to its extreme surface-sensitivity and simple construction.[1–4] The SPR-based sensor technique is based on the utilization of a noble metal to generate a surface plasmon electromagnetic field which is then used to probe changes in the optical properties, *e.g.*, by a binding reaction, that occurs within the proximity of the surface. Although the sensitivity of the SPR technique is sufficient for monitoring most analytes of interest, the detection of small molecules or trace amounts of analytes (that is, when small changes in the optical properties) continues to be a challenging task[5] because only insignificant changes in the SPR signal are observed in these cases.

We noticed that, because a probe in SPR spectroscopy is an interfacial electric field and is spatially distributed with decaying exponentially from the metal surface (Scheme 1(a)),[6] a certain matrix with spatially distributed binding sites (ligands) for recognition and binding of the analytes (the ions or molecules) to be sensed plays an integral role of probing electric fields (Scheme 1(b)), then this integration by the matrix must be sufficient to induce significant changes in the optical constants (dielectric constants), thereby resulting in more pronounced changes in the SPR response which could be readily observable. Therefore, robust and spatially extended mesoporous silica thin films were utilized as a signal amplifier to increase the sensitivity of conventional SPR.

In general, surfactant-templated mesoporous thin films[7] make for an attractive host for separations, selective catalysis and sensors due to both their physical attributes and their simple bottom-up solution phase self-assembly process.[8] Mesoporous silica thin films have been shown to provide an entry to the fabrication of versatile adaptive surfaces capable of responding to a wide variety of analytes by organosilane-based self-assembly technique.[9]



Scheme 1 (a) The intensity profile of a surface plasmon with the evanescent field extending into the dielectric medium in contact with the metal layer. (b) Schematic cartoon of the interfacial architecture of an analyte–receptor interaction in mesoporous silica thin films. The decaying length of the field, δ_d, which is of the order of half the wavelength of light involved, is comparable to the thickness *d* of mesoporous silica thin films.

The mesoporous silica thin films (MTF) used in this work were formed on a thin Au layer through the spin-coating of a self-organized mixture of hydrolyzed silicon alkoxide and a non-ionic structure directing agent. The coating solutions were prepared by the addition of an ethanol solution of PEO_{20}–PPO_{70}–PEO_{20} (Pluronic P123, M_{av} = 5800) triblock copolymer to silica sol–gels made under acid-catalyzed conditions[10] with heating a mixture of a calculated amount tetraethoxysilane (TEOS), ethanol, water and HCl at 45 °C for 1 h.

Fig. 1(a) shows a scanning electron microscopy (SEM) image of a cross section of the cast film after solvent extraction. The ∼200 nm thick film is dense, continuous, and homogeneous on the Au thin layer. A minor corrugation of the surface of the film can be seen. Transmission electron micrographs (TEM) of a detached fragment (Fig. 1(b)) shows a mesopore of 4 nm ordered into a hexagonal arrangement, which is consistent with the result obtained from the N_2 adsorption and desorption isotherms based on a BJH fit to the adsorption branch from concomitantly prepared powder samples.

The most straightforward way to investigate signal amplification by the introduction of MTF is to observe the change in SPR angle shift in the absence and in the presence of MTF when the same molecule is immobilized onto these two substrates with similar population density. For this purpose, we selected $HS(CH_2)_3Si(OCH_3)_3$ (MPTMS) because it is known to form a

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School of Chemical and Biological Engineering, Seoul National University, San 56-1, Shilim-dong, Kwanak-gu, Seoul, Korea.
E-mail: jyi@snu.ac.kr; Fax: 82-2-885-6670; Tel: 82-2-880-7438

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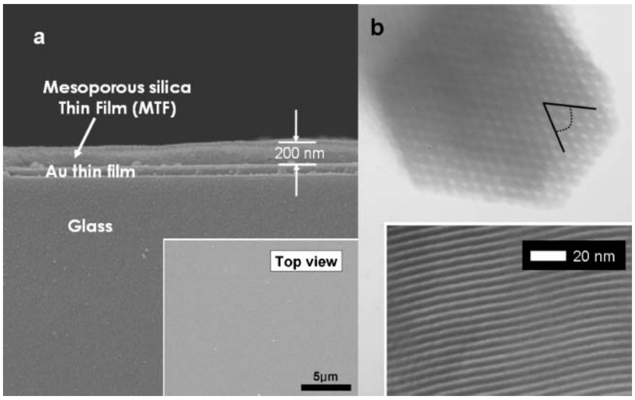

Fig. 1 (a) A cross-sectional SEM photographs of the cast film after solvent extraction with different viewing directions. (b) TEM images of the detached fragments of MTF recorded along the [100] and [110] (inset) zone axes of solvent-extracted MTF.

self-assembled monolayer (SAM) on both a Au and a silica surface. The SPR curves of the bare Au film and the MTF-modified Au thin film are characterized by a sharp plasmon minimum at an angle of 32.1 and 33.4° as shown in Fig. 2. Exposure of the bare MTF-derivatized Au film to MPTMS (Fig. 2(b)) results in a significant increase in the plasmon angle shift of 6.0° without a significant degree of plasmon damping and broadening of the curve. In contrast, a somewhat smaller angle shift of 0.08° in the SPR curve is observed upon the exposure of an identically prepared Au surface without MTF to MPTMS (control experiment). The introduction of MTF on the Au thin layer leads to significantly (~70 fold) larger changes in the corresponding SPR curves than those observed in the absence of MTF.

The theoretical amplification factor was also approximated, based on the assumption that the change in SPR response is closely associated with changes in the effective refractive index (RI) of the medium in contact with the metal surface. The effective RI was calculated by averaging the RI over the depth of the entire layer structure, always weighting the local RI with factor $[\exp(-z/\delta_{\mathrm{d}})]^2$. This average is therefore calculated with the depth integral.[11]

$$n_{\mathrm{eff}} = \frac{2}{\delta_{\mathrm{d}}}\int_0^{\infty} n(z)\exp(-2z/\delta_{\mathrm{d}})\mathrm{d}z \tag{1}$$

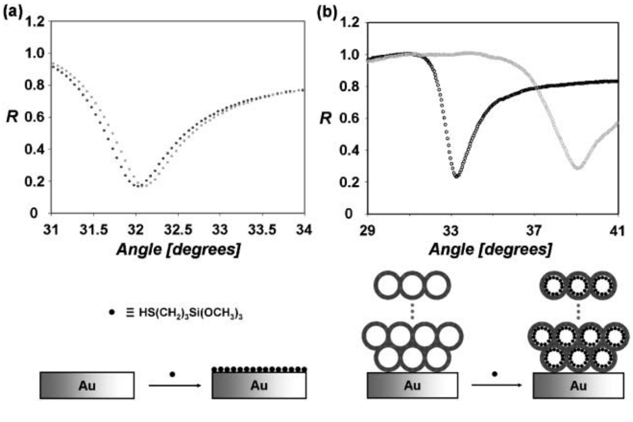

Fig. 2 Angle-resolved SPR curves and corresponding surface status of Au thin layers after the self-assembly of $HS(CH_2)_3Si(OCH_3)_3$ (3-mercaptopropyltrimethoxysilane, MPTMS) in the absence (a) and in the presence (b) of MTF with the thickness of 200 nm. All SPR spectra were taken in air.

Because the change in RI is solely induced by the immobilization of MPTMS on both substrates, Δn_{eff} is defined here as the RI change only to the self-assembly of MPTMS. For thiol-SAMs formed on Au, the typical surface density of molecules (when maximum coverage is obtained) is $\sim 4.5 \times 10^{18}$ molecules m^{-2}.[12] The population density of MPTMS on the MTF-derivatized Au thin film for a 100% coverage is 200 times larger than that on the bare Au film. The stoichiometry was based on the measured surface area (450 $\mathrm{m}^2\ \mathrm{g}^{-1}$) and the assumption of 5×10^{18} molecules m^{-2} in a fully dense monolayer coverage on the mesoporous silica surface.[12,13] Furthermore, for calculation simplicity we assumed that within MTF, an MPTMS layer with a population of 4.5×10^{18} molecules m^{-2} was repeated at 1 nm intervals (nominal direction to the metal surface). Upon this assumption, the integral of eqn (1) reduces to eqn (2)

$$\Delta n_{\mathrm{eff}} \cong \frac{2}{\delta_{\mathrm{d}}}\sum_{z=0}^{\infty}\Delta n(z)\exp(-2z/\delta_{\mathrm{d}}) \tag{2}$$

For a single recognizable layer (SAM) (in the absence of MTF), Δn_{eff} (SAM) = $2\Delta n_{z=0}/\delta_{\mathrm{d}}$, whereas, for mesoporous silica thin films, Δn_{eff} (MTF) = $(2/\delta_{\mathrm{d}})\Delta n + (2/\delta_{\mathrm{d}})\Delta n\exp(-2/\delta_{\mathrm{d}}) + (2/\delta_{\mathrm{d}})\Delta n\exp(-4/\delta_{\mathrm{d}}) + \cdots + (2/\delta_{\mathrm{d}})\Delta n\exp(-398/\delta_{\mathrm{d}}) = (2/\delta_{\mathrm{d}})\Delta n(1 - \exp(-2/\delta_{\mathrm{d}})^{200})/(1 - \exp(-2/\delta_{\mathrm{d}}))$ ($\because$ within MTF, Δn at 1 nm intervals of nominal direction is identical). Therefore, by solving this geometrical progression with a reasonable estimate that δ_{d} equals 37 ± 13% of the wavelength of the incident light (635 nm), The theoretical enhancement factor, Δn_{eff} (MTF)/Δn_{eff} (SAM) = $(1 - \exp(-2/\delta_{\mathrm{d}})^{200})/(1 - \exp(-2/\delta_{\mathrm{d}}))$ in the range of 71–110 is obtained.[14] Although the SPR angle change is a nonlinear function of the RI change with that the differences (the RI change) become larger,[11] the introduction of MTF on the Au film increases the RI change by a factor of from 71 to 110, in satisfactory agreement with the experimental results.

Demonstration of an extremely straightforward but highly sensitive SPR spectroscopy, based on the concept of extended robust binding matrix of MTF, is the most significant result. This successful combination offers all the repetitively tested features of MTF and immediately opens a massive amount of sensing opportunities for SPR spectroscopy. In addition, we expect that unlike polymer-based films, MTF (~200 nm) with an adjustable pore size (up to 30 nm), of course, minimizes the diffusion of the analyte (diffusion coefficients in an aqueous solution $D \sim 10^{-5}\ \mathrm{cm}^2\ \mathrm{s}^{-1}$) within the MTF layer and, hence, shortens the response time.

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