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Letter to the Editor

Abstract

An organic functionalized mesoporous silica substrate on a gold film enhances the sensitivity of surface plasmon resonance (SPR) spectroscopy due to its high surface area, to which more receptor molecules can be attached, compared to a general self-assembled monolayer (SAM) substrate on a gold film.

Keywords: Surface plasmon resonance; Mesoporous silica; Sensitivity enhancement; Pt detection

Enhancement of surface plasmon resonance (SPR) signals using organic functionalized mesoporous silica on a gold film

Surface plasmon resonance (SPR) spectroscopy is a powerful tool based on the refractive index change on a solid/liquid interface [1–3]. SPR spectroscopy involves the use of molecule/receptor interactions at a metal layer (e.g., gold layer) deposited on a glass prism such as antibody–antigen reactions. SPR spectroscopy has many advantages in sensor applications such as real-time, label-free and non-destructive detection, compared with other sensor techniques [4]. The resolution of SPR spectroscopy, however, is relatively low compared with other types of spectroscopy. Therefore, applications of SPR spectroscopy as a sensor are limited to some high concentration of analytes. Typically, a self-assembled monolayer (SAM) [5] of receptor molecules is used as a substrate in SPR spectroscopy. Since receptor molecules are assembled on the flat gold surface of the opposite side of the glass prism through which incident light can enter, the number of receptor molecules may be insufficient for detecting target molecules. For this reason, the SPR signal may be small in the case of low-level detection. In order to improve this resolution limit and enhance the SPR signal, novel substrates with higher concentrations of receptor molecules must be developed.

Polymers, which have many functional groups, represent candidates for the enhanced SPR substrates [6]. However, polymer structures are somewhat flexible and the structure of the polymer itself can change after the reaction of the receptor and target molecules. This structure change as well as receptor/target reactions can have an influence on the SPR signals. Therefore, an SPR signal, which is acquired by using polymer substrates, cannot be analyzed as a receptor/target reaction only, thus leading to a quantification problem. For this reason, we have investigated a porous inorganic material which has a rigid body compared with polymers as a candidate for advanced substrates to enhance the SPR signals.

It has been reported that ordered mesoporous silica generally has a uniform pore structure and monodispersed pore size (e.g., MCM-48, SBA-15) [7–9]. In addition, ordered mesoporous silica has a large surface area and a high pore volume. This large surface area and high pore volume of mesoporous silica and the inorganic rigidness present a potential use as an SPR substrate for signal enhancement. In contrast to SAM substrates which contain only one layer of receptor molecules on the surface of a gold film, mesoporous silica as an SPR substrate can have a large number of receptor molecules in the pore like multi-layers of receptor molecules. For this reason, porous inorganic materials such as mesoporous silica could be used as novel SPR substrates for enhancing SPR signals. To the best of our knowledge, the combination of mesoporous silica and SPR spectroscopy has not been reported yet, and this study is the first attempt.

Mercaptopropyltrimethoxysilane (MPTMS), 1,6-hexanedithiol (HDT) and anhydrous toluene were used as purchased from Aldrich. SBA-15 was chosen among various types of mesoporous silicas in this experiment. Typically, SBA-15 has hexagonally arranged pores of 7–8 nm size. Its surface area and pore volume were reported to be 721 m^2/g and 0.85 cm^3/g in our previous study [10]. The preparation of SBA-15 has been described in the literature [10]. In order to attach receptor molecules to the surface of SBA-15, a grafting reaction using MPTMS was used. The hybridization method for inorganic and organic materials such as grafting has been described in the literature [11,12]

This organic functionalized SBA-15 could be introduced on an Au substrate for SPR spectroscopy. The preparation of SPR Au substrates has been described elsewhere [13–15] MPTMS on the surface of SBA-15 contains a thiol group and interacts strongly with Au, so that MPTMS-grafted SBA-15 could be

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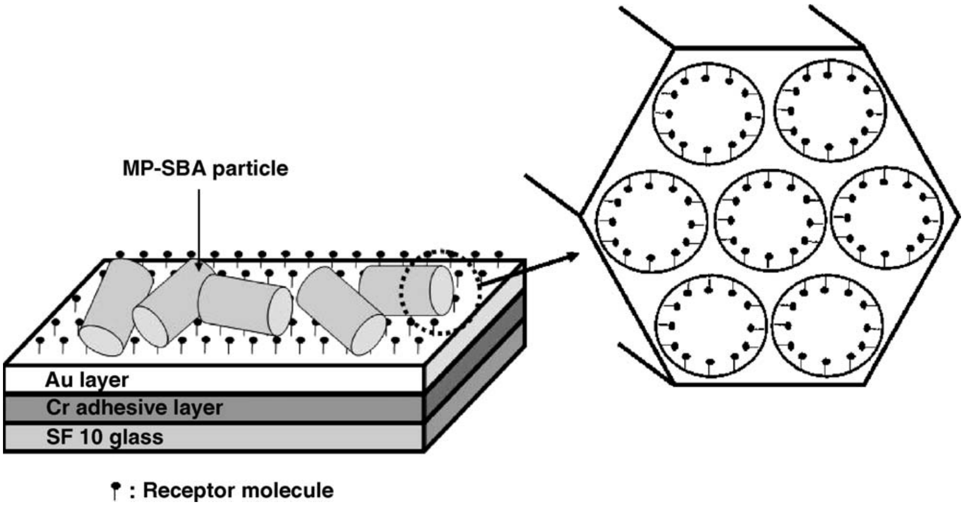

Fig. 1. Scheme of prepared support using organic functionalized mesoporous silica (SBA-15) on the Au film.

easily attached on an Au film. Being such large particles, they may not cover compactly the whole area of the Au substrate compactly. In order to introduce receptor molecules on this residual area, the prepared substrate was immersed in a 1 mM HDT solution for 4 h. This substrate, denoted as the MP-SBA substrate, was washed with ethanol and dried in air. The MP-SBA substrate is described in Fig. 1. For comparison, another substrate was prepared by the SAM method using only an HDT solution according to a procedure described in the literature [13]. This substrate is denoted as the HDT SAM substrate.

SPR measurements were carried out by using the Kretschmann configuration [16] and a monochrome laser with a 635 nm incident wavelength. The prepared substrate was attached to a SF10 prism with an index matching liquid. A Teflon cell was interfaced with the substrate to hold a Pt solution for in-situ detection. The cell had an o-ring in the middle through which laser light came into contact with the substrate. Both the prism and the cell were mounted on a rotating plate to control the angles of the incident light. In addition, prior to the measurement of the in-situ detection of Pt, the prism was rotated to determine the resonance angle where surface plasmon was at a minimum under water in the cell. All experiments were performed at room temperature.

The two substrates prepared (MP-SBA and HDT SAM) were used to detect Pt ions in the solution to compare the sensitivity. The ability to detect Pt ions could be evaluated by the angle shift after the interaction of Pt ions and the receptor molecules, (thiol groups), in the surface of the substrates. Various concentrations of Pt ions were used in the range from 10^{-5} to 1 mM. Each substrate, MP-SBA and HDT SAM, was immersed in the Pt solution for 24 h. After the complete reaction of Pt ions and the thiol groups on the surface of individual substrates, they were washed with deionized water and dried for a day.

Fig. 2 shows the angle shifts after the adsorption of Pt ions at various concentrations using both the MP-SBA and HDT SAM substrates. From the result, the MP-SBA substrate exhibits a larger angle shift than HDT SAM at all concentrations of Pt ions. Even at 10^{-5} mM, the angle shift using MP-SBA substrate (0.16°) is three times larger than that using HDT SAM (0.05°). This enhancement in SPR signal can be explained by the following theoretical base [17,18].

In general, the SPR angle, which exhibits minimum reflectance, can be represented by the following equation [17].

$$\sin \Theta_{\mathrm{SPR}} \cong \frac{n_{\mathrm{s}}}{n_{\mathrm{p}}} \tag{1}$$

where n_{s} is the refractive index of the sensing layer and n_{p} the refractive index of the prism. The refractive index of the prism remains unchanged during the detection of Pt ions, and therefore the SPR angle shift can be represented by the following simple relation [18].

$$\Delta\Theta_{\mathrm{SPR}} \propto \Delta n_s = n_{\mathrm{final}} - n_{\mathrm{initial}} \tag{2}$$

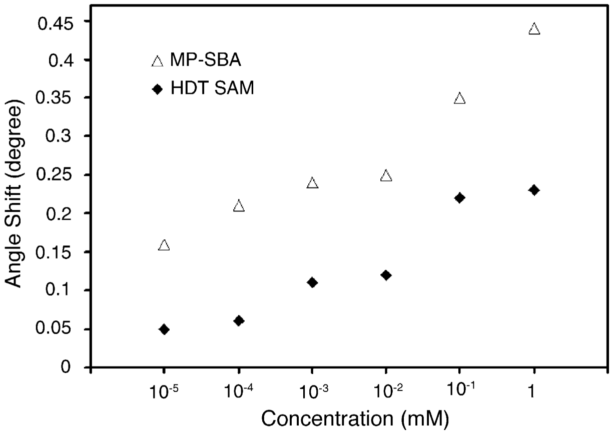

Fig. 2. SPR angle shifts in various Pt concentrations using MP-SBA and HDT SAM sensing layers.