Molecular Selectivity Development of Teflon® AF1600-coated Gold-deposited Surface Plasmon Resonance-based Glass Rod Sensor

Masaru MITSUSHIO*, Akimichi NAGAURA, Toshifumi YOSHIDOME, and Morihide HIGO

Department of Chemistry, Biotechnology, and Chemical Engineering, Graduate School of Science and Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan

* Corresponding author. Tel.: +81 99 285 8342; fax: +81 99 285 8342.

E-mail address: mitsushio@cb.kagoshima-u.ac.jp (M. Mitsushio).

ABSTRACT

A gold (Au)-deposited surface plasmon resonance (SPR)-based glass rod sensor coated with an α -mercaptoethyl- ω -methoxy polyoxyethylene (PEG thiol) layer and a Teflon AF1600 overlayer with high selectivity for small molecules in aqueous solutions was developed. The PEG thiol layer forms a space (approximately 13 nm thick) for analytes between the Au film (45 nm thick) and the Teflon layer (25 μ m thick). Small molecules in sample solutions pass selectively through the porous Teflon, accumulate in the PEG thiol layer and are detected using the SPR phenomenon. PEG thiol adsorption on the Au films was confirmed by the sensor response and X-ray photoelectron spectroscopy. Teflon overlayer thicknesses on the Au films were measured using cross-sectional scanning electron microscope images of the sensor. The sensor's selectivity was evaluated using aqueous solutions of methanol, ethanol, propanol, ethylene glycol, glycerin, pentaerythritol, and glucose. Only the monohydric alcohols pass through the Teflon overlayer, while the polyhydric alcohols do not pass through the layer. This sensor thus allows us to measure the ethanol concentrations directly in aqueous ethanol solutions mixed with interference compounds. The sensor is unaffected by glucose, tartaric acid, and glutamic acid in the solutions. (190 words)

Keywords: Au-deposited SPR glass rod sensor; Teflon AF1600 coating; PEG thiol spacer layer; molecular selectivity; monohydric alcohol.

1. Introduction

Surface plasmon resonance (SPR) sensor systems use metal films deposited on bulk prisms or optical waveguides, and use an optical phenomenon in which incident light excites charge density waves at the interface between the metal and a dielectric [1–5]. The resonance angle or the wavelength at which the coupling of the incident light and the surface plasmon waves occurs depends on both the dielectric constant of the deposited metal and the refractive index of the sample. Because the SPR sensor system only responds to the refractive index of the sample under test, many researchers have attempted to add selectivities for specific analytes to these systems [1–3,6–15]. Combination of the SPR sensor with a biochemical reaction, *e.g.*, an antigen-antibody reaction or an enzyme reaction, allows the detection of specific molecules [1–3,7,12]. Selective layers for the SPR sensing elements using an acid-base reaction [10], complex formation between an ionophore and a metal ion [11,13], molecularly imprinted polymers [8,9,15], and diffusion in agar [14] were also investigated. However, these biochemical and chemical selective layers have short lifetimes because they degenerate.

Teflon AF1600 and AF2400, commercialized by Du Pont Co., Ltd. [16], are random copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole [17–23]. They are glassy materials with large free volumes that are attributed to the amorphous parts formed by the dioxole units in the chemical structures [17]. They have extremely high gas permeability and are characterized by very large free volumes with radii of 3–8 Å [18,21]. Therefore, Teflon AF1600 and AF2400 are used as molecular sieves for sensing elements. Kurauchi *et al.* [24] fabricated a fiber-optic ethanol sensor coated with a chitosan/poly (vinyl alcohol) blended polymer membrane and a Teflon AF1600 overlayer. The Teflon layer allows the ethanol to be separated from shochu, sake, wine, whiskey, and beer. This sensor measures changes in the light intensity passing through the optical fiber as a result of an increase in the fiber critical angle caused by ethanol, which was induced by

shrinkage of the chitosan/poly (vinyl alcohol) blended membrane. The refractive indices of the thin AF1600 and AF2400 membranes are 1.31 and 1.29 refractive index (RI) units, respectively, and are lower than those of any other polymers [16]. This means that AF1600 and AF2400 can effectively be used as selective layers for the SPR sensing element. Podgorsek *et al.* [25–27] studied a silver-based SPR sensing element using the AF1600 thin film as a sensitive layer for aromatic vapors of benzene, toluene, and xylene. They calculated the diffusion coefficients of these aromatic vapors in the AF1600 film. Erickson *et al.* [28] reported a gold-based near-infrared SPR sensing system with an oxygen plasma-etched Teflon AF1600 selective layer to detect benzene, toluene, and xylene in water. They demonstrated detection limits for benzene, toluene, and xylene of 183, 105, and 55 parts per billion (ppb), respectively.

We previously developed a small and simple Au-deposited multimode optical fiber sensor, in which the light intensity of a He–Ne laser (632.8 nm) that was transmitted through the sensor was measured without scanning of the wavelength or variation of the angle of incidence of the light [29–40]. Another simple sensor system using Au-deposited glass rods with diameters of 1–4 mm and deposition lengths of 10–100 mm equipped with a light-emitting diode (LED) has also been presented [41,42]. The response properties of these metal-deposited optical fiber and glass rod sensors could be controlled by varying the metal thickness [32–35,40], the type of metal used [36–38,40], and the incident light wavelength [39–41]. Recently, we have developed a Teflon AF1600-coated Au-deposited SPR-based optical fiber sensor [43]. This sensor allows us to measure ethanol concentrations directly in shochu, sake, and wine. Experiments showed that the ethanol concentrations could be measured directly in a mixture containing glucose or tartaric acid. The ethanol solution sensitivity of the sensor was enhanced by adding an α -mercaptoethyl- ω -methoxy polyoxyethylene (PEG thiol) spacer layer between the Au film and the Teflon selective layer.

This paper describes in detail the response properties of a Teflon AF1600-coated

Au-deposited SPR-based glass rod sensor. The adsorption behavior of the PEG thiol layer on the Au films and the morphology of the Teflon AF1600 film on the SPR glass rod sensor are also discussed. The PEG thiol adsorption behavior was monitored using the response of the sensor without the Teflon layer to an ethanol solution of PEG thiol. The adsorption and monolayer formation of PEG thiol on the Au films [44–47] was also confirmed using X-ray photoelectron spectroscopy (XPS). The formation of the Teflon overlayers on the sensors was observed by scanning electron microscopy (SEM) and the layer thicknesses were measured from their cross-sectional images. The responses of the Teflon AF1600-coated Au-deposited SPR-based glass rod sensor to aqueous ethanol solutions were observed. The sensor's selective properties were evaluated using aqueous solutions of methanol, ethanol, propanol, ethylene glycol, glycerin, pentaerythritol, and glucose. The sensor allows us to perform direct measurements of the ethanol concentrations of aqueous ethanol solutions mixed with glucose, tartaric acid, and glutamic acid. The results demonstrated the value of the Teflon AF1600-coated Au-deposited SPR glass rod sensor with molecular size selectivity.

2. Principle

Figure 1 shows a schematic representation of the response principle of the Teflon AF1600-coated Au-deposited SPR glass rod sensor. The chemical structures of PEG thiol and Teflon AF1600 are also shown. The sensing element has a silicate glass rod/Au film/PEG thiol spacer layer/Teflon AF1600 overlayer structure. Teflon AF1600 is composed of amorphous random copolymers of 65 mol% 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and 35 mol% tetrafluoroethylene, and exhibits strong hydrophobicity. The radii of the free volume elements in the Teflon AF film are in the 3–8 Å range [18,21]. The Teflon AF film shows size-sieving properties and high gas and liquid permeability because of its large free volume [17–23].

It is well known that thiol forms a self-assembled monolayer on Au [44–47]. The PEG thiol layer acts as a hydrophilic spacer between the Teflon AF1600 overlayer and the Au film [43]. Thus, the small hydrophilic molecules that have been selected by the Teflon layer accumulate in the PEG thiol spacer layer and are detected as a change in the refractive index of the layers through the SPR phenomenon on the Au film deposited on the silicate glass rod.

3. Experimental

The preparation of the Au-deposited SPR glass rod sensor elements has been reported previously [41,42]. The Au film with a thickness of 45 nm was deposited on half of the clean silicate glass rod (2 mm diameter $\times$ 140 mm long, Vidtec, Fukuoka, Japan) by Au (>99.99%, Ishifuku Metal, Tokyo, Japan) evaporation at a rate of 1.0 nm/s in a high vacuum ($<6 \times 10^{-4}$ Pa) at room temperature. The Au film deposited on the glass rod has a geometrical thickness distribution in which the maximum value (45 nm) represents the deposited metal thickness [35–43]. The uncertainty of the Au film thickness was less than 0.3 nm. The Au-deposited glass rod was then immersed into a 0.1 mM ethanol solution of PEG thiol (ME-050SH, MW: 5,000, NOF Corporation, Tokyo, Japan) for 1 h to form the spacer layer. After the adsorption of PEG thiol on the Au film of the Au-deposited glass rod, the rod was washed thoroughly with ethanol and dried for 30 min in the air. Finally, the Au-deposited glass rod with the adsorbed PEG thiol layer was coated with a Teflon overlayer, which was fabricated by either five or six repeated cycles of immersion of the Au-deposited glass rod into a 35 mg/ml Fluorinert (FC-72, Sumitomo 3M, Tokyo, Japan) solution of Teflon AF1600 (DuPont, Wilmington, Delaware, USA) followed by drying for 1 min. The sensor element and the Teflon tubes that were used as the sample inlets and outlets were fixed in a glass tube (5 or 6 mm diameter, 120 mm long) with resin to form a sensor cell. Sample solutions at 25°C were then allowed to flow through the sensor cell.

One end of the glass rod of the sensor element was illuminated using an LED (SLA-560LT, 654 nm emission wavelength, Rohm, Kyoto, Japan) and the transmitted light intensity through the sensor was monitored using either a photodetector (S2386-44K, Hamamatsu Photonics, Shizuoka, Japan) or an optical multimeter (OMM-6801B, ILX Lightwave, Bozeman, Montana, USA) equipped with a Si detector (VOMM-6722B, ILX Lightwave). The light intensity was also converted into digital data by a digital multimeter (755501-1, Yokogawa, Tokyo, Japan) that was used as an analog-to-digital (A/D) converter and was then monitored by a computer (PC-9821 Xs, NEC, Tokyo, Japan) via an RS-232C connection. The sample refractivities were measured with an Abbe refractometer (DR-A1, Atago, Tokyo, Japan), and the measurement uncertainties were less than 2×10^{-4} RI units.

The X-ray photoelectron spectra of adsorbed PEG thiol on Au films deposited on slide glasses were measured with an ESCA-1000 (Shimadzu, Kyoto, Japan) using non-monochromated Mg K α radiation (1253.6 eV). The photoelectrons that were emitted normal to the surface (3×10 mm²) were analyzed with a resolution of 1.1 eV. The binding energy was calibrated to the Au 4f_{7/2} line at 84.0 eV. The SEM images were taken with an E-SEM XL30CP (Philips, Amsterdam, Netherlands) at an acceleration voltage of 5 kV. The SEM observation samples were coated with Au using a sputter coater (SC7610, Quorum Technologies, East Sussex, England) at pressures in the 4–6 Pa range. The contact angles of water (50 μ l) on the Au surfaces were measured from pictures taken with a digital camera.

4. Results and Discussion

4.1. Adsorption of PEG thiol on the Au film

In our previous paper, it was shown that the ethanol solution sensitivity of the Au-deposited

SPR optical fiber sensor coated with the Teflon AF1600 overlayer was enhanced by the presence of the PEG thiol spacer layer between the Au film and the overlayer [43]. Figure 2 shows the PEG thiol adsorption behavior on the Au surface of the SPR glass rod sensor. The 0.1 mM ethanol solution of PEG thiol flowed into the sensor cell for 95 min after an ethanol flow for 5 min. The ethanol solution of PEG thiol circulated through the sensor cell during the adsorption process. The transmitted light intensity of the sensor was normalized relative to the intensity for ethanol at 0 min. A small reduction in the light intensity observed during the flow of ethanol was caused by a change in the room temperature. When the sample was changed to the ethanol solution of PEG thiol, the transmitted light intensity decreased immediately because of the PEG thiol adsorption on the Au surface of the sensor. Because of the strong adsorption of the PEG thiol monolayer, the transmitted light intensity showed no more significant changes after 60 min had passed. However, because the change in the response after 60 min in contact with the ethanol solution of PEG thiol was small, the adsorption time of 60 min was determined to be sufficient to form the spacer layer.

The XPS spectra of the PEG thiol on the Au films that were deposited on the slide glasses were measured to confirm the formation of the PEG spacer layer. The wide spectra of the unmodified Au film (a) used for reference and the Au film immersed in the 0.1 mM ethanol solution of PEG thiol for 60 min (b) are shown in Fig. 3. In the XPS spectrum of the unmodified Au film (a), very strong peaks assigned to Au 4f, medium peaks for Au 4d and 4p, and a quite weak peak for C 1s are observed [48,49]. After the PEG thiol adsorption on the Au film (b), peaks for C 1s, O 1s, and O Auger arise at the corresponding binding energies in the XPS spectrum. The peaks related to the elements of C and O in the spectrum (b) can be ascribed to the adsorption of PEG thiol. However, no peak for S of the adsorbed PEG thiol is observed. The Au 4f, 4d, and 4p peaks weaken because of the formation of the PEG thiol layer on the Au film. The relative peak intensities (0.025 ± 0.014) of Au 4f before and after the formation of the PEG spacer layer provided a rough layer thickness estimate of approximately 13 nm based on the inelastic mean free path (3.3

nm) of the photoelectrons from Au [45].

The narrow spectra of O 1s and C 1s in Fig. 3(b) are shown in Fig. 4. The spectrum of O 1s has a sharp and symmetrical peak at 532.7 eV, while that of C 1s has a strong peak at 286.8 eV and a very weak shoulder at approximately 285 eV. Cacao *et al.* [47] reported narrow XPS spectra of O 1s and C 1s from PEG thiol (MW: 5,000) adsorbed on Au deposited on a Si wafer using a high resolution of 0.51 eV. The O 1s spectrum has a single peak at approximately 532 eV. The C 1s spectrum has a major peak corresponding to the ether bonding state at 286.6 eV and the alkyl peak at 284.6 eV. The O 1s spectra of adsorbed PEG thiols with shorter PEG chains on Au also showed a peak at 533 eV [46]. The C 1s spectra of adsorbed PEG thiols with similar molecular structures on Au showed two peaks at 286.5–286.8 and 284.9–285.0 eV [44–46]. The XPS narrow spectra shown in Fig. 4 agreed well with spectra of similar PEG thiols on Au reported in the literature [44–47]. The water contact angles for the Au films before ($74.6 \pm 2.4^\circ$) and after ($16.4 \pm 3.3^\circ$) immersion in the PEG thiol solution also indicated the formation of the hydrophilic spacer layer on the surface.

It has also been reported that PEG thiols adsorbed on substrates have various helical, zigzag, or random conformations on the surfaces, which depend on the molecular structures, the lengths of the PEG chains, and the substrates [44–47]. A conformation in a crystalline PEG chain is essentially a (7/2) helix structure in which the seven monomeric units with heights of 1.948 nm turn twice [50]. Assuming that the conformation of the PEG that is adsorbed on the Au film has a (7/2) helix structure and that it is adsorbed normal to the surface, the PEG layer thickness is estimated to be approximately 30 nm, and is thicker than that (approximately 13 nm) measured by XPS. Because the PEG thiol layer is thicker than the inelastic mean free path (3.3 nm) of the photoelectrons from Au [45], the Au peak intensities weaken. No peak related to S was observed because PEG thiol is adsorbed at the S atom on the Au surface, and the PEG chain length is considered to be much longer than the inelastic mean free path of the photoelectrons from the S atom.

4.2. Teflon AF1600 overlayer and its thickness

Typical cross-sectional SEM images of the elements of the Teflon AF1600-coated Au-deposited SPR glass rod sensors are shown in Fig. 5. The Au film (45 nm) and the PEG spacer layer (approximately 13 nm) are too thin to be observed in these images. The number of cycles of immersion into the Fluorinert solution of Teflon and the drying process were 2 cycles (a) and 5 cycles (b). All images were taken from the sensors that were actually used in this study. The average thicknesses of the Teflon films on the Au films were calculated from nine cross-sectional SEM images, and the thicknesses for images (a) and (b) are 8.3 ± 0.7 and 24.7 ± 5.0 μm , respectively. Thus, the Teflon layer is formed at a rate of 4–5 μm per immersion and drying cycle. In the preliminary experiment for formation of the Teflon layer on the Au-deposited SPR glass rod sensor, the selectivity of the sensing element formed using fewer than five immersion cycles was insufficient for use with aqueous ethanol solutions with glucose. It was found that the Teflon AF1600 layer thickness needs to be approximately 25 μm to add the molecular size selectivity property to this sensing element.

4.3. Response of sensor coated with PEG thiol and Teflon AF1600 to ethanol solutions

Figure 6 shows the response curve of the Au-deposited SPR glass rod sensor with the PEG thiol spacer layer and the Teflon AF1600 overlayer to various concentrations of the aqueous ethanol solutions. The data were recorded at intervals of 1 s. The transmitted light intensities for the sensor were normalized relative to those for water at 0 min. The samples were exchanged every 8 min. The change in the light intensity indicates that the ethanol and the water diffuse into the Teflon film, and reach the spacer layer in the SPR sensing region on the Au film. When the samples flowed into the sensor cell, the transmitted light intensity began to change within a few minutes.

The transmitted light intensity of the sensor shows a reversible response to the sample concentration, and returned to its initial value for an exchange of a sample for water after 16 min.

Figure 7 shows the responses (a) and their rates (the numerical differential coefficients) (b) of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to aqueous ethanol solutions of 10, 30, and 50%, v/v. The transmitted light intensities for the sensor were normalized relative to those for water at 0 min. The vertical solid lines shown in (a) represent the times where the response rates became less than -0.1 min^{-1} . The data were recorded every 0.25 s and the response rates were calculated every 1 min. First, water was flowed into the sensor cell over a period of 5 min, and then the responses for the samples were measured. The sensor response increased as the ethanol concentration of the sample increased. Because all the response rates became less than -0.1 min^{-1} after 15 min in Fig. 7(b), the response of this sensor to each sample was measured 15 min after introduction of the sample into the sensor cell.

4.4. Selective response properties of the sensor coated with PEG thiol and Teflon AF1600

The response properties of the sensor coated with PEG thiol and Teflon AF1600 for 5%, w/w aqueous solutions of ethanol (1), ethylene glycol (2), glycerin (3), pentaerythritol (4), and glucose (5) are shown in Fig. 8. The responses of the unmodified sensor to the same samples are also shown. The transmitted light intensities for the sensor were normalized relative to those for water (0). The unmodified sensor clearly responded to the refractive indices of the sample solutions. However, the sensor coated with the PEG thiol and Teflon layers only showed a response to the aqueous ethanol solution. This sensor also showed responses to 5%, w/w aqueous solutions of methanol, 1-propanol, and 2-propanol. These results showed that only the monohydric alcohols pass through the Teflon overlayer, while the polyhydric alcohols do not pass through the layer.

Figure 9 shows the responses of the unmodified Au-deposited SPR glass rod sensor to aqueous ethanol solutions with and without glucose interference. Glucose at 5.0%, w/w was added to the aqueous ethanol solutions. The transverse axes of (a) and (b) represent the aqueous ethanol solution concentrations and the refractive indices of the samples, respectively. The transmitted light intensity for each sample was normalized relative to that for the solvent (distilled water) at 1.333 RI units. Because the unmodified Au-deposited SPR glass rod sensor has no selectivity for aqueous ethanol solutions, the sensor responses to the aqueous ethanol solutions with glucose content are larger than those for the aqueous ethanol solutions without glucose (a). However, the sensor clearly responds to the total refractive indices of the aqueous ethanol solutions with glucose content (b).

Figure 10 shows the responses of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to the same samples that were used in Fig. 9. The transverse axes of (a) and (b) also represent the aqueous ethanol solution concentration and the refractive index of the sample, respectively. While the response of this sensor is smaller than that of the unmodified sensor because the Au surface is coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer, it has selectivity for aqueous ethanol solutions. This sensor shows that the glucose has no influence on the response to the aqueous ethanol solution (a). The deviations between the responses to samples with and without glucose content over 12 measurements were less than or equal to 1%. The identical responses of the sensor to each of the aqueous ethanol solutions with and without glucose show that the sensor responds only to the refractive indices of the aqueous ethanol solutions (b). The sensor also showed no response to glucose (1.5%, w/w), tartaric acid (1.0, w/w), and glutamic acid (0.25, w/w) in the aqueous ethanol solutions.

5. Conclusions

In this study, we have presented a simple and effective way to provide molecular size selectivity for our Au-deposited SPR-based glass rod sensor. The Teflon AF1600 layer has a porous structure and it allows molecules that are smaller in size than the free volume element in the Teflon to pass through. The sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer shows a reversible response to the concentrations of monohydric alcohols. Only ethanol and water in the sample solutions mixed with interference compounds with larger molecular sizes pass through the porous structure of the Teflon selective layer with the thickness of 25 μm , and they accumulate in the PEG thiol spacer layer with the thickness of approximately 13 nm. The accumulated aqueous ethanol solutions can be detected selectively and sensitively via the SPR phenomenon on the Au film deposited on the silicate glass rod within 15 min. Because this is a unique sensor with functions of both separation and detection of analytes, and because the Teflon membrane has a low refractive index, high chemical stability, and a long lifetime, this sensor is expected to be used for applications in, *e.g.*, environmental monitoring, lubricant degeneration detection, and the sake brewing industry.

Acknowledgements

The authors would like to thank Miss K. Matsuo and Miss K. Anayama for their cooperation in conducting this work. The present study was partially supported by a grant from the Iketani Science and Technology Foundation (No. 0191009-A), and by the Project to Develop “Innovative Seeds” (No. 16-032) and the Technology Transfer and Innovation Program (2007) from the Japan Science and Technology Agency.

References

- [1] J. Homola, S. S. Yee, G. Gauglitz, *Sens. Actuators B* 54 (1999) 3.
- [2] H. Muguruma, *Bunseki* (2003) 38.
- [3] J. Homola, *Anal. Bioanal. Chem.* 377 (2003) 528.
- [4] X. Liu, D. Song, Q. Zhang, Y. Tian, L. Ding, H. Zhang, *Trends Anal. Chem.* 24 (2005) 887.
- [5] A. K. Sharma, R. Jha, B. D. Gupta, *IEEE Sens. J.* 7 (2007) 1118.
- [6] P. A. Drake, P. W. Bohn, *Anal. Chem.* 67 (1995) 1766.
- [7] S. Nishimura, *Bunseki Kagaku* 50 (2001) 79.
- [8] S. Nishimura, T. Yoshidome, M. Higo, *Anal. Sci. Suppl.* 17 (2001) i1697.
- [9] S. Nishimura, T. Yoshidome, M. Higo, *Bunseki Kagaku* 50 (2001) 733.
- [10] S. Nishimura, T. Yoshidome, T. Tokuda, M. Mitsushio, M. Higo, *Anal. Sci.* 18 (2002) 261.
- [11] S. Nishimura, T. Yoshidome, W. Kyuutoku, M. Mitsushio, M. Higo, *Anal. Sci.* 18 (2002) 267.
- [12] S. Nishimura, W. Kyuutoku, M. Mitsushio, T. Yoshidome, M. Higo, *Bunseki Kagaku* 51 (2002) 163.
- [13] K. Kurihara, K. Nakamura, E. Hirayama, K. Suzuki, *Anal. Chem.* 74 (2002) 6323.
- [14] M. E. Montecillo, T. Yoshidome, T. Yamagata, T. Yamasaki, M. Mitsushio, B. J. Sarno, M. Higo, *Bull. Chem. Soc. Jpn.* 83 (2010) 1531.
- [15] Q. Wei, T. Wei, X. Wu, *Chem. Lett.* 40 (2011) 132.
- [16] Du Pont-Mitsui Fluorochemicals Company, "Product Information Teflon AF", available from (http://www.md-fluoro.co.jp/products/fluoropolymer/product_info/af.html), (accessed 2014 10 9).
- [17] I. Pinnau, L. G. Toy, *J. Membrane Sci.* 109 (1996) 125.
- [18] A. M. Polyakov, L. E. Starannikova, Yu. P. Yampolskii, *J. Membrane Sci.* 216 (2003) 241.
- [19] A. M. Polyakov, L. E. Starannikova, Yu. P. Yampolskii, *J. Membrane Sci.* 238 (2004) 21.

- [20] A. Polyakov, G. Bondarenko, A. Tokarev, Yu. Yampolskii, *J. Membrane. Sci.* 277 (2006) 108.
- [21] H. Zhang, A. Hussam, S. G. Weber, *J. Am. Chem. Soc.* 132 (2010) 17867.
- [22] M. C. Ferrari, M. Galizia, M. G. De Angelis, G. C. Sarti, *Ind. Eng. Chem. Res.* 49 (2010) 11920.
- [23] M. O'Brien, L. R. Baxendale, S. V. Ley, *Org. Lett.* 12 (2010) 1596.
- [24] Y. Kurauchi, T. Yanai, N. Egashira, K. Ohga, *Anal. Sci.* 10 (1994) 213.
- [25] R. P. Podgorsek, T. Sterkenburgh, J. Wolters, T. Ehrenreich, S. Nischwitz, H. Franke, *Sens. Actuators B* 38-39 (1997) 349.
- [26] R. P. Podgorsek, H. Franke, *Appl. Phys. Lett.* 73 (1998) 2887.
- [27] R. P. Podgorsek, H. Franke, *Appl. Opt.* 41 (2002) 601.
- [28] T. A. Erickson, R. Nijjar, M. J. Kipper, K. L. Lear, *Talanta* 119 (2014) 151.
- [29] M. Mitsushio, S. Kamata, *Bunseki Kagaku* 48 (1999) 757.
- [30] M. Mitsushio, T. Yoshidome, S. Kamata, *Bunseki Kagaku* 49 (2000) 307.
- [31] M. Mitsushio, S. Higashi, M. Higo, *Anal. Sci. Suppl.* 17 (2001) i1721.
- [32] M. Mitsushio, S. Higashi, M. Higo, *Bunseki Kagaku* 52 (2003) 433.
- [33] M. Mitsushio, S. Higashi, M. Higo, *Anal. Sci.* 19 (2003) 1421.
- [34] M. Mitsushio, S. Higashi, M. Higo, *Sens. Actuators A* 111 (2004) 252.
- [35] M. Mitsushio, M. Higo, *Anal. Sci.* 20 (2004) 689.
- [36] M. Mitsushio, K. Miyashita, M. Higo, *Sens. Actuators A* 125 (2006) 296.
- [37] M. Mitsushio, K. Watanabe, Y. Abe, M. Higo, *Sens. Actuators A* 163 (2010) 1.
- [38] M. Mitsushio, Y. Abe, M. Higo, *Anal. Sci.* 26 (2010) 949.
- [39] M. Mitsushio, M. Higo, *Anal. Sci.* 27 (2011) 247.
- [40] M. Mitsushio, M. Higo, *Bunseki Kagaku* 61 (2012) 999.
- [41] M. Mitsushio, M. Higo, *Opt. Commun.* 285 (2012) 3714.
- [42] M. Mitsushio, T. Masunaga, M. Higo, *Plasmonics* 9 (2014) 451.

- [43] M. Mitsushio, T. Mukano, M. Higo, *Bunseki Kagaku* 63 (2014) 365.
- [44] P. Harder, M. Grunze, R. Dahint, G. M. Whitesides, P. E. Laibinis, *J. Phys. Chem. B* 102 (1998) 426.
- [45] H. B. Lu, C. T. Campbell, D. G. Castner, *Langmuir* 16 (2000) 1711.
- [46] M. Cerruti, S. Fissolo, C. Carraro, C. Ricciardi, A. Majumdar, R. Maboudian, *Langmuir* 24 (2008) 10646.
- [47] E. E. Cacao, A. Nasrullah, T. Sherlock, S. Kemper, K. Kourentzi, P. Ruchhoeft, G. E. Stein, R. C. Willson, *PLOS ONE* 8 (2013) e56835.
- [48] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, "Handbook of X-ray Photoelectron Spectroscopy", 1979, Perkin-Elmer Corporation Physical Electronics Division, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344 USA.
- [49] B. V. Crist, "Handbooks of Monochromatic XPS Spectra, Volume 1 – The Elements and Native Oxides", 1999, XPS International Inc., 3408 Emerald Drive, Ames, Iowa, 50010 USA.
- [50] Y. Takahashi, H. Tadokoro, *Macromolecules* 6 (1973) 672.

Figure Captions

Fig. 1. Schematic representation of the response principle of the Au-deposited SPR glass rod sensor coated with an α -mercaptoethyl- ω -methoxy polyoxyethylene (PEG thiol) layer and a Teflon AF1600 overlayer. Small molecules in the sample solution pass through the porous structure of the Teflon AF1600 selective layer with the thickness of 25 μm , and they accumulate in the PEG thiol spacer layer with the thickness of 13 nm. The accumulated small molecules are detected selectively and sensitively via the SPR phenomenon on the Au film deposited on the silicate glass rod.

Fig. 2. Response of the Au-deposited SPR glass rod sensor during adsorption of PEG thiol on the

Au film of the sensor from a 0.1 mM ethanol solution. The transmitted light intensity of the sensor was normalized relative to that for ethanol at 0 min.

Fig. 3. XPS wide spectra of Au films deposited on slide glasses before (a) and after (b) immersion into a 0.1 mM ethanol solution of PEG thiol for 60 min. The C 1s and O 1s peaks of the adsorbed PEG thiol were observed with the weak peaks of Au. No peak was observed for S from the adsorbed PEG thiol.

Fig. 4. XPS narrow spectra of O 1s and C 1s for the Au film deposited on the slide glass after immersion into a 0.1 mM ethanol solution of PEG thiol for 60 min. The spectral line shape of O 1s at 532.3 eV is symmetrical. The C 1s line has a strong peak at 286.8 eV and a very weak shoulder at approximately 285 eV.

Fig. 5. Cross-sectional SEM images of the Teflon AF1600-coated Au-deposited SPR glass rod sensors. The immersion and drying process cycles for the Teflon AF1600 solutions were carried out two (a) and five times (b). The SEM image magnification is 1000 $\times$.

Fig. 6. Response of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to aqueous ethanol solutions ranging from 0 to 50%, v/v. The samples were exchanged every 8 min.

Fig. 7. Responses (a) and their rates (b) of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to the aqueous ethanol solutions of 10, 30, and 50%, v/v. The broken line represents the rate of -0.1 min^{-1} .

Fig. 8. Responses of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to 5%, w/w aqueous solutions of ethanol (1), ethylene glycol (2), glycerin (3), pentaerythritol (4), and glucose (5). The responses of the unmodified sensor to the same samples are also shown. The broken line represents the response of the sensor to water (0).

Fig. 9. Responses of the unmodified Au-deposited SPR glass rod sensor to aqueous ethanol solutions with and without the addition of glucose (5%, w/w). The transverse axes of (a) and (b) represent the aqueous ethanol solution concentration and the refractive index of the sample, respectively. The sensor has no selectivity for aqueous ethanol solutions and simply responds to the refractive indices of the samples.

Fig. 10. Responses of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF1600 overlayer to aqueous ethanol solutions with and without the addition of glucose (5%, w/w). The transverse axes of (a) and (b) represent the aqueous ethanol solution concentration and the refractive index of the sample, respectively. The sensor has selectivity for aqueous ethanol solutions and responds to the refractive indices of the aqueous ethanol solutions only.

Teflon AF1600

PEG thiol (M.W. $\approx$ 5000, $n \approx$ 110)

Teflon AF1600

PEG thiol (M.W. $\doteq$ 5000, $n \doteq$ 110)

Fig. 1 Mitsushio et al.

Fig. 2 Mitsushio et al.

Fig. 3 Mitsushio et al.

Fig. 4 Mitsushio et al.

(a)

(b)

Fig. 5 Mitsushio et al.

Fig. 6 Mitsushio et al.

Fig. 7 Mitsushio et al.

Fig. 8 Mitsushio et al.

Fig. 9 Mitsushio et al.

Fig. 10 Mitsushio et al.