Separation and Detection of Hydrocarbons and Gasoline in Automotive Engine Oil Using a Teflon® AF2400-coated Gold-deposited Surface Plasmon Resonance-based Glass Rod Sensor

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A gold (Au)-deposited surface plasmon resonance (SPR)-based glass rod sensor that is coated with an α -mercaptoethyl- ω -methoxy polyoxyethylene (PEG thiol) layer (approximately 13 nm thick) and a Teflon AF2400 overlayer (12 μ m thick) was used to detect the hydrocarbon and gasoline contents of automotive engine oil. Hydrocarbons and gasoline present in the engine oil penetrate through the porous Teflon layer and accumulate in the PEG thiol layer, and are then detected using the SPR sensor. The refractivities of the selective layers that contain a hydrocarbon on the Au-deposited glass rod sensor were estimated from the sensor responses when using light-emitting diodes (LEDs) with various operating wavelengths as light sources. Gasoline concentrations up to 10%, w/w in commercial engine oil can be measured directly using this sensor when it is coated with the selective layers. The responses of an SPR-based optical waveguide sensing system using Au films coated with identical selective layers were also measured. The results demonstrate the value of the Au-deposited SPR glass rod sensor coated with the selective layers for the detection of the gasoline content and fuel dilution of automotive engine oil.

Keywords Au-deposited SPR-based glass rod sensor, Teflon AF2400, engine oil, hydrocarbon, gasoline, fuel dilution

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Introduction

Condition monitoring of automotive engine oil contaminated by fuel, coolant, and water has been receiving increasing attention in recent years.¹⁻⁶ The contamination of this oil by unburned fuel is generally the first and most dominant cause of engine oil degradation.³⁻⁶ Oil exchange timing is determined not by the lubrication performance deterioration but by time or mileage. It is thus highly desirable to detect these contaminants and monitor the degree of the fuel dilution of engine oil. Spectroscopic monitoring methods of the degradation and the fuel dilution of the engine oil are difficult, because the degraded engine oil becomes dark and the transparency decreases.^{1,2} Methodologies to detect the contaminants based on the distortion effect when an object image is obtained through a thin layer of the engine oil have been proposed.^{2,5} The ability of these systems to distinguish up to 10% contaminants in engine oil was verified experimentally.^{2,5} A fast device for determining the degree of fuel dilution of engine oil with gasoline and diesel based on viscosity changes has been developed.³ The device allowed to perform an express analysis of the dilution of working engine oil with fuel. A monitoring system for fuel dilution of engine oil with diesel has been developed using a quartz crystal

resonator.⁶ Achievable detection limits were below 0.5% fuel concentrations in the oil.

Surface plasmon resonance (SPR) is a coupling between a charge density wave existing on a metal surface and a wave vector of light that is parallel to the metal surface.⁷⁻¹⁰ In general, a sample/metal/prism or a sample/metal/waveguide structure, which is called the Kretschmann configuration, is used to excite the SPR. The SPR-based sensor allows a rapid, non-destructive, remote, and continuous analysis. Zhan *et al.*¹¹ developed a portable-type SPR sensor consisting of a light emitting diode (LED), various lenses, a prism, a polarizer, and a linear CCD array. The sensor allows to measure a change of the refractive index (RI) with a detection limit of $3.2 - 5.5 \times 10^{-5}$ RI units. Shinbo *et al.*¹² developed a waveguide SPR sensor with dual sensing parts, and poly(acrylic acid) and poly(vinyl alcohol) were used as sensing layers for NH₃ gas. The combination measurement of these layers allows highly sensitive detection of NH₃ gas under various humidity conditions. The degradation of engine oil by gasoline, coolant, and water using traditional SPR measurements was studied by Aghayan *et al.*¹⁴ They reported that the introduction of these contaminants to engine oil leads to noticeable changes in the resonance angle and the minimum reflectivity of the SPR curve due to an increase in the dielectric permittivity. Though their works are evaluated as the first attempts of using SPR for condition monitoring of engine oil, the development of a compact and selective SPR sensor system is strongly desired.

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Unmodified SPR sensing elements allow the RI of a material sample to be determined with high accuracy. Because the SPR sensing elements only respond to the RI of the sample, various attempts have been made to impart selectivities for specific analytes to these sensing elements.^{7,8} Teflon AF1600 and AF2400 are glassy materials that consist of random copolymers of 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole and tetrafluoroethylene.^{13–16} These materials have large free volumes with radii of 3 – 8 Å in their amorphous parts, which are formed by the dioxole units.^{15,16} While both Teflon AF1600 and AF2400 have extremely high gas and liquid permeabilities because of their large free volumes, AF2400 has higher permeabilities than AF1600.^{13–15} The thin AF1600 and AF2400 membranes have refractivities of 1.31 and 1.29 RI units, respectively,¹³ and they can be used effectively as selective layers for the SPR sensing elements. Kurauchi *et al.*¹⁷ fabricated a fiber-optic ethanol sensor coated with a chitosan/poly(vinyl alcohol) blended polymer membrane and a Teflon AF1600 overlayer. Podgorsek *et al.*^{18–20} and Erickson *et al.*²¹ studied SPR sensing elements that have an AF1600 sensing layer on the SPR active metal. These sensing elements allowed to detect benzene, toluene, and xylene content in head space gas or water. These aromatic compounds were detected using traditional SPR sensors that were coated with the AF1600 layers; however, no attempts have been made to separate or detect individual molecules that have been mixed into solutions.

Optical fiber or glass rod sensor systems based on SPR offer a unique technique and enable continuous analysis, remote sensing, and *in situ* monitoring using small, low-cost, and disposable sensor elements.^{7–10,22–40} A simple sensor system that used Au-deposited glass rods (with diameters of 1 – 4 mm and deposition lengths of 10 – 100 mm) and was equipped with a light-emitting diode (LED) was also presented.^{33,35,39} The responses of these metal-deposited glass rod sensors could be controlled by the thickness of the metal layer^{35,39} and the incident LED light wavelength.³³ We developed a Au-deposited optical fiber sensor or glass rod sensor that was coated with an α -mercaptoethyl- ω -methoxy polyoxyethylene (PEG) thiol layer and a Teflon AF1600 or AF2400 overlayer.^{36–38,40} The PEG thiol spacer layer enhances the sensitivity of these sensors by accumulating the molecules in the layer, which penetrate through the Teflon layer.^{36–38} These sensors allowed us to measure the ethanol concentrations in shochu, sake, and wine directly, along with coexisting substances, *e.g.*, sugars and organic acids.^{36,38} It has been shown that these sensors, when coated with the PEG thiol layer and the Teflon overlayer, provide high selectivity for sensing of small alcohol molecules in various aqueous solutions.^{37,38} Further investigations of the separation and detection of other analytes in various solutions when using these sensors are both interesting and important in terms of understanding of the operating mechanism of these unique Teflon selective layers. We have preliminarily reported a measurement method for the fuel dilution of engine oil using metal-deposited SPR-based glass rod sensors coated with a PEG thiol spacer layer and either a Teflon AF1600 or AF2400 overlayer.⁴⁰ The response time of the Teflon AF2400-coated sensor was faster than that of the Teflon AF1600-coated sensor as a result of the higher permeability and the reduced thickness of the Teflon AF2400 overlayer.³⁸ These sensors enable us to measure the gasoline content in engine oil selectively and directly.

This paper describes the response characteristics of a Au-deposited SPR glass rod sensor that was coated with a PEG thiol spacer layer and a Teflon AF2400 overlayer to detect gasoline in commercial automotive engine oil. Comparisons with the response characteristics of unmodified sensors showed

that the selective layers effectively perform the tasks of separation and detection of the gasoline contained in the engine oil. The responses of the sensor that was coated with these selective layers to various hydrocarbons that were mixed into the engine oil were also observed. The refractivities of the selective layers when they contained a hydrocarbon on the Au-deposited glass rod sensor were estimated based on the responses when using LEDs with various wavelengths. Concentrations up to 10%, w/w of the gasoline mixed into the engine oil could be measured directly using this sensor when coated with these selective layers. The responses to hydrocarbons and gasoline mixed into engine oil were also measured for an SPR-based optical waveguide sensing system that used Au films coated with the same selective layers. These results demonstrated the value of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer for engine oil condition monitoring applications. The proposed sensor allows us to construct a practical sensing system for the fuel dilution of engine oil.

Experimental

We have previously reported the fabrication processes for the Au-deposited SPR glass rod sensors coated with the PEG thiol spacer layer and a Teflon overlayer.^{37,38} The Au film (which was 100 nm long) has a geometrical thickness distribution in which the maximum value of 45 nm was deposited over half of the clean silicate glass rod surface (2 mm diameter $\times$ 150 mm long; Vittec, Fukuoka, Japan) by Au (>99.99%; Ishifuku Metal, Tokyo, Japan) evaporation at a rate of 1.0 nm/s under a high vacuum ($<6 \times 10^{-4}$ Pa) at room temperature. The uncertainty of the resulting film thickness was less than 0.3 nm. The spacer layer on the Au film was then formed by immersing the Au-deposited glass rod into a 0.1 mM ethanol solution of PEG thiol (ME-050SH, MW: 5000; NOF Corporation, Tokyo, Japan) for 1 h. After the PEG thiol spacer layer (approximately 13 nm thick) was formed on the Au film on the Au-deposited glass rod, the rod was washed thoroughly in ethanol and dried for 30 min in air. Finally, a Teflon overlayer (12 μ m thick) was fabricated on the Au-deposited glass rod with the PEG thiol spacer layer by seven repeated cycles in which the Au-deposited glass rod was immersed into a 35 mg/ml Fluorinert (FC-3283; 3M Japan, Tokyo, Japan) solution of Teflon AF2400 (DuPont, Wilmington, Delaware, USA) and then dried for 1 min. The Teflon tubes that were used as sample inlets and outlets and the sensor element were all fixed in a glass tube (5 mm diameter, 120 mm long) using resin to form the sensor cell. Sample solutions of hexane, octane, decane, and gasoline mixed in engine oil that were maintained at 25°C were then flowed through the sensor cell. The base oil was offered by Nissan Motor, Kanagawa, Japan. Commercial engine oil (Nissan Strong Save X 5W-30; Nissan Motor, Kanagawa, Japan) was also used.

Figure 1 shows a schematic representation of the sensor system composed of the Au-deposited SPR glass rod sensor that was coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer. One end of the glass rod of the sensor element was illuminated using a yellow LED (YCL-513UYC-TS, 591 nm emission wavelength; Kaito Denshi, Saitama, Japan), a red LED (SLA-560LT, 654 nm emission wavelength; Rohm, Kyoto, Japan), or an infrared LED (OSIR5113A, 934 nm emission wavelength; OptoSupply, Hong Kong, China). Both the light intensities that were transmitted through the sensor and those from the LEDs were monitored using an optical power meter that was equipped with a Si detector (Labmaster Ultima,

Fig. 1 Schematic representation of the experimental setup for the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer, comprising a light-emitting diode (LED) light source, Si detectors for both response and reference signals, and a sensor cell containing the sensor element. The sensor element is the Au-deposited SPR glass rod, which has a diameter of 2 mm, a deposition length of 100 mm, and Au film thickness of 45 nm, and is coated with the spacer layer (approximately 13 nm thick) and the Teflon overlayer (12 μm thick). The responses were corrected using normalized light intensities from the reference signals.

Coherent, California, USA) to be used as the response and reference signals, respectively. These light intensities were recorded using a computer *via* an RS-232C interface at intervals of 1 s. The responses were corrected using the normalized light intensities from the reference signal. A signal (S) was defined as the difference between the average values of the responses to the engine oil (0%) before sample introduction and the response to the sample solution after they reached constant levels over a period of 0.5 min. The noise (N) was the sum of the standard deviations of the stabilized responses before and after the change in the sample. The sample refractivities were also measured using an Abbe refractometer (RX-5000 α -Bev; Atago, Tokyo, Japan), and the measurement uncertainties were less than 2×10^{-5} RI units. The responses of unmodified Au-deposited SPR glass rod sensors without the additional selective layers were also measured using the three LEDs operating in the refractivity range from 1.327 to 1.422 RI units with methanol solutions of ethylene glycol.

The responses to specific hydrocarbons (hexane, octane, decane, dodecane, benzene, toluene, and *p*-xylene) and gasoline mixed into commercial engine oil were also observed using an existing SPR optical waveguide sensing system (SIS-5000; System Instruments, Hachioji, Tokyo, Japan). A Au film (45 nm thick, with dimensions of $3 \times 18 \text{ mm}^2$) on a glass slide ($18 \times 18 \text{ mm}^2$, $n_d = 1.5220$; Muto Pure Chemicals, Tokyo, Japan) that was coated using the same selective layers on a waveguide ($n_d = 1.80610$; Sumita Optical Glass, Saitama, Japan) with matching oil ($n_d = 1.5220$; Moritex, Saitama, Japan) was used. Sample solutions (100 μl) contained in a liquid cell on the Au film made from a silicone rubber sheet with a cover to prevent evaporation of either the hydrocarbons or the gasoline were measured at room temperature. The response of the SPR sensing system is represented by a peak shift in the SPR wavelength spectrum relative to the sample solution from the engine oil.

Results and Discussion

Responses to hydrocarbons in engine oil

The bulk of typical gasoline consists of hydrocarbons that

Fig. 2 Typical response curves for the Au-deposited SPR glass rod sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer to solutions of hexane, octane, and decane when mixed in commercial engine oil at concentrations ranging from 0 to 10%, w/w. The transmitted light intensities of the sensor were normalized with respect to that for commercial engine oil at 0 min. The samples were changed every 20–25 min.

contain between 4 and 12 carbon atoms per molecule (C4 – C12) and is thus a mixture of alkanes, cycloalkanes, and alkenes. The actual ratio depends on the refinery that produced the gasoline, the crude oil used, and the grade of the gasoline. Gasoline also contains other organic compounds, including aromatic hydrocarbons, ethers, and alcohols, which are used as additives. The responses of the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer to some of the hydrocarbons that are mixed into commercial engine oil were observed. The responses of the SPR optical waveguide sensing system that used Au films coated with the same selective layers to the various hydrocarbons that were mixed into commercial engine oil were also measured.

Figure 2 shows the typical response curves of the Au-deposited SPR glass rod sensor that was coated with the spacer layer and the Teflon overlayer to various concentrations (% w/w) of hexane, octane, and decane in commercial engine oil when using a red LED (654 nm). The samples were changed every 20–25 min. The reflectance of an inner surface of the sensor based on the SPR is affected by the refractive index of the sample on the Au film. Thus, a change in the light intensity indicates that the hydrocarbon has diffused into the Teflon film and reached the PEG thiol spacer layer in the SPR sensing region on the Au film.^{36–38} The transmitted light intensities of the sensor were normalized with respect to that measured for the commercial engine oil at 0 min. These intensities began to change within a few minutes of the sample initially flowing into the sensor cell. The sensor response to each sample stabilized

Fig. 3 Typical responses of the Au-deposited SPR glass rod sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer to solutions of hexane, octane, and decane mixed in commercial engine oil (a) and those of the SPR optical waveguide sensing system (SIS-5000) to solutions of hexane, octane, decane, and dodecane in commercial engine oil (b), with concentrations ranging from 0 to 10%, w/w. The uncertainties of these responses at the concentration of 10%, w/w are shown.

within a few minutes of the initial introduction of the sample into the sensor cell. The sensor response to the sample concentration is reversible and did return to its initial value, but the response time required to return from the response to a 10% solution to that for the commercial engine oil (0%) was very long (more than 50 min). It is much longer than the response time of a sensor coated with the same selective layers to aqueous ethanol solutions (which was approximately 5 min). The sensor response shows a molecular size dependence and it decreases as the number of carbon atoms in the hydrocarbon increases.

Figure 3(a) shows the responses of the Au-deposited SPR glass rod sensor that was coated with the spacer layer and the Teflon overlayer to various concentrations (% w/w) of hexane, octane, and decane that were mixed into the commercial engine oil. The responses of the SPR optical waveguide sensing system that used Au films coated with the same selective layers for these hydrocarbons to dodecane mixed into the commercial engine oil were also measured. The SPR optical waveguide sensing system's responses to the concentrations of hydrocarbons mixed into the commercial engine oil that are shown in Fig. 3(b) correlate well with those of the Au-deposited SPR glass rod sensor (shown in Fig. 3(a)). The response of the sensing system

Fig. 4 Typical responses of the SPR optical waveguide sensing system (SIS-5000) to solutions of benzene, toluene, and *p*-xylene when mixed in commercial engine oil with concentrations ranging from 0 to 10%, w/w. The uncertainties of the responses at the concentration of 10%, w/w are shown to be less than 1 nm.

is also dependent on the molecular size and it decreases as the number of carbon atoms in the hydrocarbon increases.

The responses of the SPR optical waveguide sensing system that used Au films coated with the same selective layers to some aromatic hydrocarbons were also measured. Figure 4 shows the responses of this sensing system to benzene, toluene, and *p*-xylene mixed into the commercial engine oil. Similar responses to those of the sensor to these aromatic hydrocarbons were observed. Both the Au-deposited SPR glass rod sensor and the SPR optical waveguide sensing system that used the Au films coated with the same selective layers showed no responses to the engine oil. These observations indicate that the hydrocarbons also diffuse into the Teflon film and thus reach the PEG thiol spacer layer in the SPR sensing region on the Au film, as per the case of monohydric alcohols in water.^{36–38} It is believed that the diffusion of the larger hydrocarbons into the Teflon film becomes more difficult as the hydrocarbons increase in size, and less accumulation occurs in the spacer layer than it would for the smaller hydrocarbons.

Estimation of the refractivities of the sensing region using various LEDs

The response characteristics of the metal-deposited SPR optical fiber and glass rod-type sensors can be controlled by varying the wavelength of the incident LED light.^{32,33} The refractivities of the SPR sensing region when it contained a hydrocarbon on the Au film of the Au-deposited SPR glass rod sensor that was coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer were estimated based on their responses to three LEDs with different operating wavelengths.

Figure 5 shows the typical response curves of the Au-deposited SPR glass rod sensor when coated with the spacer layer and the Teflon selective layer that were measured using LEDs with operating wavelengths of 591 nm (yellow) and 934 nm (infrared) to concentrations ranging from 0 to 10%, w/w of hexane in commercial engine oil. The response curve of the same sensor when using the LED operating at 654 nm (red) is also shown. The transmitted light intensities of the sensor in each case were normalized with respect to that for the oil at 0 min. The *S/N* ratio of the response curve of the sensor that was coated with the selective layers when measured using the yellow LED is lower than the ratios that were measured using the other LEDs.

Fig. 5 Typical response curves for the Au-deposited SPR glass rod sensor coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer that were measured using three LEDs with wavelengths of 591 nm (yellow), 654 nm (red), and 934 nm (infrared) as light sources to solutions of hexane when mixed in commercial engine oil with concentrations ranging from 0 to 10%, w/w. The transmitted light intensities of the sensor were normalized with respect to that for commercial engine oil at 0 min.

This is because the attenuation properties of the SPR phenomenon are dependent on the dielectric constant (ϵ) of the deposited metal and the dielectric constant of Au when using the yellow light is not effective in producing the SPR sensor response.³³ The measured intensities are also low because the response range is around its minimum value.

The responses of the sensor that was coated with the spacer layer and the Teflon overlayer that were measured using the three LEDs to the various concentrations (0–10%, w/w) of hexane are shown in Fig. 6 (right). The responses of the sensor that was coated with the selective layers when using the red and infrared LEDs show monotonic reductions with increasing hexane concentration up to 10%, w/w. In contrast, the response of the same sensor when using the yellow LED has a minimum at a concentration of approximately 6%, w/w. Figure 6 (left) also shows the responses of unmodified sensors operating in the refractivity range of 1.327–1.422 RI units for comparison. The refractivity values at the minima of the responses that were obtained using the yellow, red, and infrared LEDs are 1.338, 1.373, and 1.421 RI units, respectively.³³ The uncertainty values are ± 0.003 RI units. Comparisons between the responses of the unmodified sensor and those of the sensor with the selective layers shown in Fig. 6 and the refractivity value (1.29 RI units) of Teflon AF2400¹³ provides an estimate of the refractivity range in the SPR sensing region of the selective layers when they contain hexane. The refractivity range in the SPR sensing region on the Au film with the PEG thiol spacer layer and the Teflon AF2400 overlayer that contains hexane in concentrations ranging from 0 to 10%, w/w in the engine oil is estimated to be 1.29–1.37 RI units. These refractivity values indicate that the hydrocarbons contained in the engine oil penetrate through the porous Teflon layer and subsequently accumulate in the PEG thiol layer, and the changes in the refractivity of the sensing region on the Au film can then be detected using the SPR phenomenon.

Fig. 6 Typical responses of the unmodified Au-deposited SPR glass rod sensor to refractivities ranging from 1.327 to 1.422 RI units and those of the same sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer to solutions of hexane when mixed in commercial engine oil with concentrations ranging from 0 to 10%, w/w. These responses were measured using three LEDs with wavelengths of 591 nm (yellow), 654 nm (red), and 934 nm (infrared) as light sources. The refractivity range in the sensing region of these selective layers on the Au film over this concentration range was estimated to be 1.29–1.37 RI units.

Fig. 7 Typical response curves for the unmodified Au-deposited SPR glass rod sensor to air and to gasoline when mixed in commercial engine oil at concentrations ranging from 0 to 10%, w/w. The transmitted light intensities of the sensor were normalized with respect to that for air at 0 min. The unmodified Au-deposited glass rod sensor shows no response to all the sample concentrations.

Separation and detection of gasoline in engine oil

The Au-deposited SPR glass rod sensor that was coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer responds effectively to the presence of the various hydrocarbons in the engine oil. An attempt to detect gasoline that had been mixed into the engine oil was therefore made.

Figure 7 shows the variation of the transmitted light intensities of an unmodified Au-deposited SPR glass rod sensor for air and for various concentrations of gasoline mixed into engine oil. The samples were changed every 2.5 min. The refractivities of the samples were 1.4660, 1.4651, 1.4638, and 1.4612 RI units for concentrations of 0, 1, 5, and 10%, w/w, respectively. The transmitted light intensities of the sensor were normalized with respect to that for air. Because the refractivities of the samples are higher than that of the glass rod (1.4562 RI units),³⁵ the incident light leaked from the glass rod directly to the sample without any total reflection process. The light intensity values were approximately 0.55 for all samples, because part of the light from the LED passes directly through the glass rod without any reflections from the inner surfaces of the glass rod. The unmodified Au-deposited glass rod sensor showed no response to all the samples. The unmodified Au-deposited glass rod sensor therefore cannot be used for direct detection of gasoline in the engine oil.

Figure 8(a) shows the response curve of the Au-deposited SPR glass rod sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer to the various concentrations of gasoline that were mixed into the engine oil. The transmitted light intensities for this sensor were normalized with respect to that for the engine oil (0%) at 0 min. When the sample solutions were introduced into the sensor cell, the transmitted light intensity of the sensor decreased within a few minutes and reached a constant value within 15 min. The sensor response showed monotonic reductions with increasing gasoline concentration. The *S/N* ratio for concentrations of between 0 and 2%, w/w was calculated to be 8.21. The detection limit for gasoline in engine oil for this sensor was estimated to be 0.49% with an *S/N* ratio of 2.0. The responses of the SPR optical waveguide sensing system when using the Au films coated with the same selective layers to the various concentrations of gasoline in the commercial engine oil are shown in Fig. 8(b). These responses correlate well with those of the Au-deposited

Fig. 8 Typical response curve for the Au-deposited SPR glass rod sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer (a) and the responses of the SPR optical waveguide sensing system (SIS-5000) (b) to gasoline when mixed in commercial engine oil at concentrations ranging from 0 to 10%, w/w. The uncertainty of the response at the concentration of 10%, w/w is shown for the SPR optical waveguide sensing system.

SPR glass rod sensor shown in Fig. 8(a).

Commercial engine oil contains many additives that are used to control its performance. The Au-deposited SPR glass rod sensor that was coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer showed no response to an anti-wear agent composed of zinc dithiophosphate (ZnDTP) that was contained in the base oil. It appears that the molecular size of ZnDTP is too large to penetrate through the porous Teflon structure, similar to the case of glucose in water.^{36–38} Sensors coated with the same selective layers also showed no response to tartaric acid,^{36–38} glutamic acid, and some alcohols (including ethylene glycol, glycerin, and pentaerythritol)^{37,38} in aqueous ethanol solutions. This indicates that the Au-deposited SPR glass rod sensor when coated with the PEG thiol spacer layer and the Teflon AF2400 overlayer can be used for direct monitoring of the degeneration of engine oil caused by fuel dilution.

Conclusions

We have demonstrated that a Au-deposited SPR-based glass rod sensor that is coated with a PEG thiol spacer layer and a Teflon AF2400 overlayer can be used for effective detection of contaminant hydrocarbons and gasoline contained in automotive engine oil. The sensor responds reversibly to various concentrations of the hydrocarbons and the gasoline. The responses of an SPR optical waveguide sensing system that used

Au films coated with the same selective layers were also observed. The refractivities in the SPR sensing region on the Au film in the selective layers on the Au-deposited glass rod sensor when they contained a hydrocarbon could be estimated based on the sensor's responses when using three LEDs with different operating wavelengths as light sources. The estimated values for the sensing region provided important information about the selectivity and responsivity of this unique sensor when coated with the spacer layer and the Teflon overlayer. Hydrocarbons and gasoline contained in the engine oil penetrated through the porous Teflon layer and accumulated in the PEG thiol layer, and the resulting changes in the refractivity in the sensing region on the Au film were then detected using the SPR phenomenon. Gasoline concentrations up to 10%, w/w in commercial engine oil could be measured directly within 15 min when using this sensor coated with the selective layers. The sensor that is proposed here is a new device that acts to both separate and detect gasoline in automotive engine oil. Because the Teflon membrane offers low refractivity, high chemical stability, and a long lifetime, this sensor is expected to be applied in areas such as lubricant degeneration detection.

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