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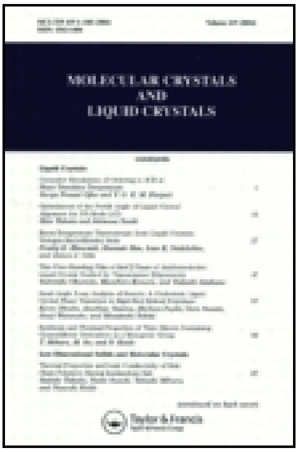

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Liquid Sensor Using Localized Surface Plasmon Resonance of Gold Nanoparticles Deposited on Polydimethylsiloxane-Based Organic-Inorganic Hybrid Materials

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Liquid Sensor Using Localized Surface Plasmon Resonance of Gold Nanoparticles Deposited on Polydimethylsiloxane-Based Organic-Inorganic Hybrid Materials

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In this paper, we fabricated gold nanoparticles (GNPs) on PDMS-based organic-inorganic hybrid materials in order to assembly liquid sensor using localized surface plasmon resonance. Using PDMS-based hybrid materials as a substrate enables us to control the structure of GNPs by synthesizing hybrid materials with the appropriate molar ratio of metal alkoxide to PDMS because the GNPs were deposited on (3-aminopropyl)triethoxysilane-modified inorganic parts of the hybrid materials by chemical adsorption. In addition, LSPR condition of GNPs deposited on the PDMS-based hybrid materials changes by not only refractive index of liquid surrounding GNPs but polarity of liquid because swelling of PDMS-based hybrid materials results in expansion of interparticle distance of GNPs. We measured absorption spectrum of GNPs as a function of time after the immersion to the liquids. We confirmed that time variation of the spectrum differs by changing the kind of sample liquid according to swelling characteristics of PDMS. This result suggests that the prepared GNPs deposited on hybrid material could work as a sensor for selective detection of the liquid sample.

Keywords Gold nanoparticles; localized surface plasmon; liquid sensor; organic-inorganic hybrids materials; polydimethylsiloxane

Introduction

Surface plasmon resonance (SPR) is the resonant, collective oscillation of valence electrons in a metal stimulated by incident light. The resonance condition is established by matching the frequency of light photons and the natural frequency of surface electrons. Localized surface plasmon resonance (LSPR) is generated around nanometer-sized structures. The LSPR condition depends on size, shape of the metal nanoparticles, and refractive index of the ambient media surrounding the metal nanoparticles.

Recently, localized surface plasmon polariton sensor has been proposed using gold colloidal monolayers deposited on glass substrate [1–3]. The sensor utilizes a property of the absorption peak of gold nanoparticles (GNPs) that is due to the LSPR. However, in such a conventional LSPR sensor, it is difficult to detect the organic solvents as a sample because the LSPR condition of GNPs deposited on glass substrate depend on only refractive index of the sample liquid surrounding the GNPs.

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In this paper, we employed the polydimethylsiloxane (PDMS)-based organic–inorganic hybrid materials as a substrate of GNPs in order to improve the selectivity of liquid sample in LSPR sensor. PDMS-based organic–inorganic hybrid materials made from PDMS and metal alkoxides by in-situ sol-gel method have characteristics in its flexibility and transparency. In particular, PDMS based-hybrid materials made of TA have a loose crosslinking structure through the inorganic particles derived from metal alkoxides [4–7], therefore the PDMS based hybrid materials can be swelled in the liquid sample. The interparticle distance of GNPs on the hybrid material can be changed and the LSPR condition can be changed by swelling of the hybrid materials. Because swelling kinetics is correlated with the molecular weight and the polarity of the liquid sample, time variation of absorption spectrum after the immersion of GNPs on the hybrid materials into liquid sample differs by changing the kind of sample liquid. Another advantage using PDMS based hybrid materials as a substrate of GNPs is that GNPs can be deposited selectively on the inorganic parts of PDMS-based hybrid materials by chemical adsorption. The aggregate size of GNPs on the PDMS-based hybrid materials is controllable by changing the molar ratio of inorganic component to organic component (PDMS). We fabricated the GNPs deposited on PDMS-based hybrid materials and investigated the time variation of the absorption spectra of GNPs after immersion into different kind of liquid samples.

Experimental

Sample Preparation

Gold nanoparticles were synthesized by chemical reduction process [8]. Citrate-stabilized gold nanoparticles were prepared by boiling a mixture of 0.56 mL of 24 mM $HAuCl_4$ solution, 1.25 mL of 38.8 mM sodium citrate solution, and 50 mL of deionized water for 10 minutes. The solution changed the color to bright red during the boiling. The solution was rapidly cooled down to the room temperature. PDMS-based hybrid materials were used as a substrate of GNPs. The PDMS-based hybrid materials were made from titanium alkoxide (TA: $Ti(OCH_2CH(C_2H_5)C_4H_9)_4$), alkoxysilane (ES: $Si_7O_6(OC_2H_5)_{16}$), and PDMS end-linked with $Si_7O_6(OC_2H_5)_{16}$ (alkoxysilane-terminated PDMS) with an average molecular weight of 27,000 [7]. The molar ratio of TA : ES : alkoxysilane-terminated PDMS was 1 : x : 1 (x = 0–1.0). The solution was allowed to gel at 150°C for 1hour and then heat-treated at 250°C for 2 hours to produce the hybrids materials, which had a crosslinking structure of PDMS through the inorganic particles derived from TA and ES. The surface of the hybrid materials are modified by (3-aminopropyl)triethoxysilane (APTMS) by dipping in a mixture of APTMS and ethanol in a molar ratio of 1 : 10. The GNPs were deposited on APTMS-modified PDMS-based hybrid materials by chemical adsorption when the hybrid materials were immersed into the GNPs aqueous dispersion for 1 hour. Excess GNPs on the hybrid materials were removed by washing carefully with deionized water and ethanol.

Characterization

The morphology was examined by atomic force microscopy (Pacific nanotechnology Nano-R). The diameter and covering ratio of GNPs on the hybrid materials were analyzed by image processing software (Image Metrology SPIP). Absorption spectra of the GNPs were measured with UV-visible absorption spectrophotometer (Shimadzu UV-160A). The absorption spectra of the GNPs on the hybrid materials immersed into several kinds of

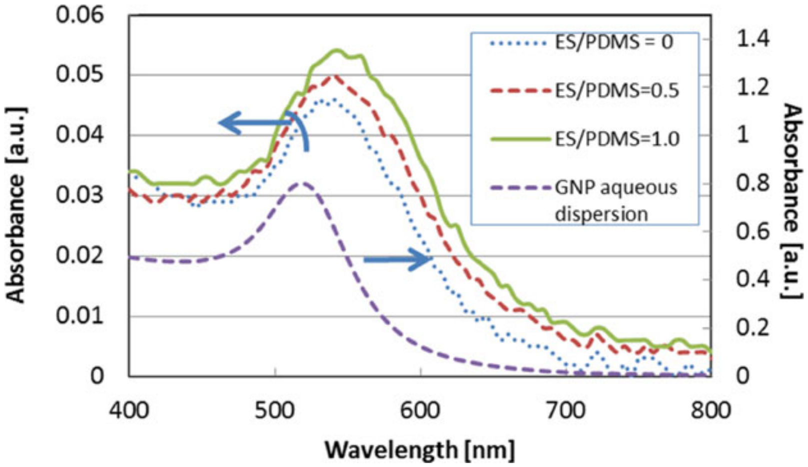
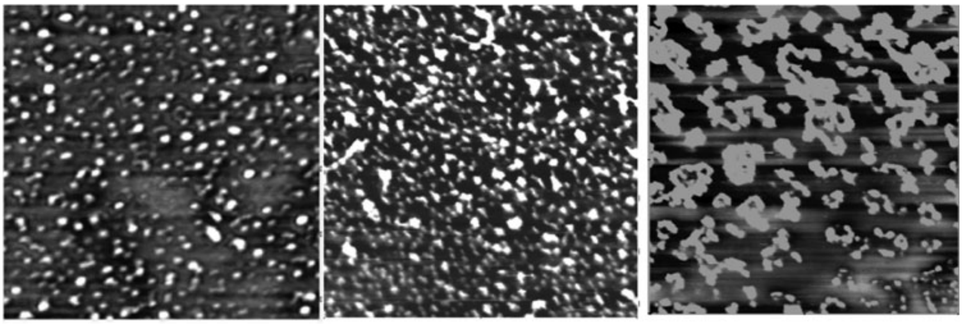


Figure 1. Absorption spectra of Au colloid solution and gold nanoparticles on PDMS-based hybrid material.

liquid samples, namely hexane (n = 1.39), toluene (n = 1.50), and iodomethane (n = 1.53) were measured. The sample was mounted on quartz cell with a 10 mm optical length. The absorption spectrum is measured as a function of immersion time.

Result and Discussion

Figure 1 shows absorption spectra of GNPs aqueous dispersion and GNPs deposited on the hybrid materials with different molar ratio of ES to PDMS. Intense absorption bands with maxima around 518 nm were observed for the spectra of GNPs aqueous dispersion because the GNPs were stabilized as dispersed particles in the solution [9]. In contrast, for GNPs on the PDMS-based hybrid materials, the broad absorption appeared on the region of wavelength longer than those of the plasmon band of GNPs aqueous dispersion because the GNPs aggregated on the hybrid materials. As the molar ratio of ES to PDMS increased, the absorbance became larger and the peak wavelength became higher for GNPs deposited on the hybrid materials. This suggests that the degree of aggregation of GNPs increased with the increasing the molar ratio of ES to PDMS. Figure 2 shows the AFM phase images of GNPs on the hybrid with different molar ratio of ES to PDMS. The size of GNP particle did not change in spite of the increase in a molar ratio of ES to PDMS, namely, the average (±standard deviation:SD) diameter of GNPs deposited on the PDMS-based hybrid material with molar ratio of ES to PDMS of 0, 0.5, and 1.0 were 16.8 ± 5.1 nm, 17.1 ± 5.1 nm, and 18.1 ± 5.5 nm, respectively. The covering ratio of GNPs on the hybrid materials with molar ratio of ES to PDMS of 0, 0.5, and 1.0 are about 18%, 37%, and 43%, respectively, and the increase in size of GNP aggregates was observed with the increase in molar ratio of ES to PDMS. These results indicated that the structure of deposited GNPs, such as covering ratio, aggregate size of GNPs, is controllable by choosing appropriate molar ratio of inorganics to PDMS. The increase in the aggregation of GNPs is believed to be due to the formation of aggregate of inorganic particle in the hybrid materials. It has been reported that the several PDMS-based hybrid materials synthesized by PDMS and metal alkoxides by sol-gel method with small molar ratio of metal alkoxides to PDMS have a network structure through the well-dispersed inorganic particles without formation of aggregate,

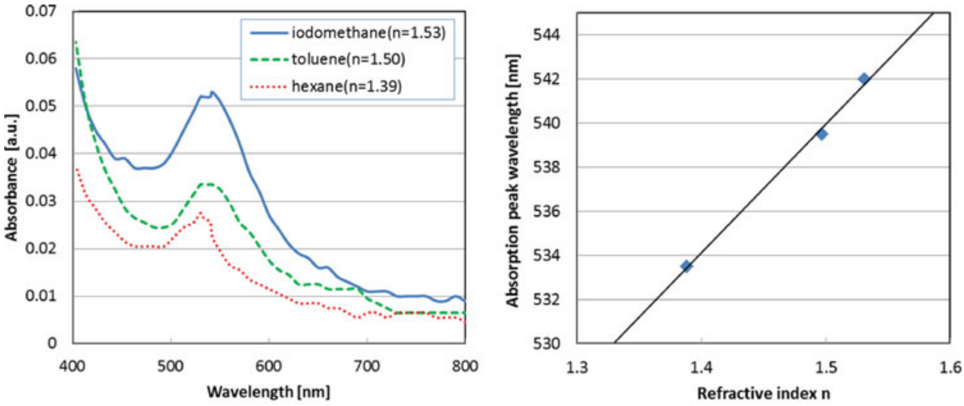


(a) (b) (c)

Figure 2. AFM phase images of GNPs on the hybrid materials with molar ratio of ES to PDMS :(a) ES/PDMS = 0, (b) ES/PDMS = 0.5, and (c) ES/PDMS = 1.0. Scanning area was 1 μm × 1 μm.

however, when the molar ratio of alkoxides to PDMS is increased above certain value, the chance of aggregate formation in structure is high. It is suspected that the PDMS-based hybrid materials made from TA, ES, and alkoxysilane-terminated PDMS with molar ratio of ES to PDMS of 1.0 and above have aggregate structure of inorganic particles.

Figure 3(a) shows absorption spectra of GNPs on the PDMS-based hybrid materials with molar ratio of ES to PDMS of 0.5, which are immersed into the liquids of different refractive indices. Here, the spectra were measured after sufficient immersion (15 minutes). The absorption peak wavelength of each GNPs on the hybrid materials is seen to be shifted to longer wavelength side as the refractive index *n* of liquid sample increased. The absorption peak wavelength shifts linearly with the change of the refractive index of liquid sample surrounding GNPs as shown in Fig. 3(b). Figure 4 shows relationships of immersion time and absorption peak wavelength of GNPs on PDMS-based hybrid materials with molar ratio of ES to PDMS of 0.5. The peak wavelength of absorption spectrum of GNPs had a characteristic value according to the refractive index of liquid surrounding



(a) (b)

Figure 3. (a) Absorption spectra of gold nanoparticles on hybrid materials with molar ratio of ES to PDMS of 0.5 in different liquids, and (b) Relationship of refractive index and absorption peak wavelength of GNPs on hybrid materials with molar ratio of ES to PDMS of 0.5.

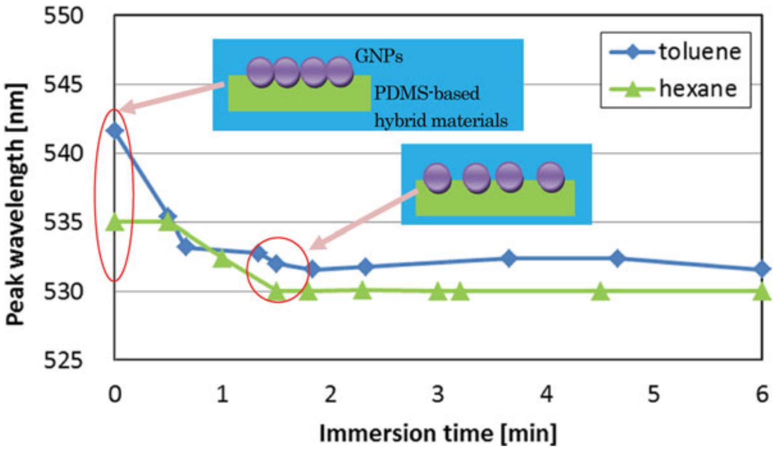


Figure 4. Absorption peak position GNPs deposited on hybrid materials with molar ratio of ES to PDMS of 0.5 vs. immersion time.

GNPs when GNPs were immersed into liquid sample. Subsequently, the peak wavelength of an absorption spectrum decreased with time, and reached the minimum value in a few minutes after immersion. However, the time to reach minimum peak wavelength (T_{min}) changed with the kinds of surrounding liquid, that is, the values of T_{min} are about 1.8 and 1.5 minutes for toluene and hexane, respectively. The decrease of peak wavelength is attributed to the change of the interparticle distance of GNPs through the swelling of PDMS. This difference in time variation according to the kind of liquids is attributed to different swelling kinetics of hybrid materials because the kinetics differs according to molecular weight and polarity of liquids. These results provide basis that GNPs on the hybrid materials are applicable for a sensor for selective detection of specific liquid sample by measuring the time variation of absorption spectrum of GNPs deposited on PDMS-based hybrid materials compared with conventional LSPR sensor.

Conclusion

We have fabricated GNPs on PDMS-based organic-inorganic hybrid materials and explored the possibility of liquid sensor using LSPR. GNPs were deposited on surface of hybrid materials by chemical adsorption. We found that degree of aggregation of GNPs is controllable by changing the molar ratio of metal alkoxide to PDMS in synthesis. We measured the absorption spectrum of GNPs, which were immersed into liquid samples, as a function of immersion time. It was demonstrated that the time variation of absorption spectrum of GNPs after the immersion changed of the kind of liquid sample surrounding GNPs according to swelling characteristics of PDMS. We confirmed that the prepared GNPs deposited on hybrid material could work as a liquid sensor for selective detection of liquid sample.

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