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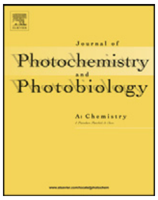

Enhanced photocycloreversion reaction of diarylethene polymers attached to gold nanoparticles in the solid state

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ABSTRACT

The photochromic reactivity of diarylethene polymers attached to gold nanoparticle in the solid state was investigated. The photochromic diarylethene polymers around the gold nanoparticle exhibited reversible photochromism upon alternating irradiation with ultraviolet (UV) and visible light even in the solid state. The local surface plasmon resonance (LSPR) band of the gold nanoparticle in the solid state was red-shifted in comparison with that dispersed in a solution because of the closer interparticle distance. Alternating irradiation with UV and visible light led to the photoreversible changes in the LSPR band because the refractive index of the diarylethene polymer shell changes along with the photochromic reaction of the diarylethene polymers. However, the behavior of the spectral changes significantly depended on the irradiation wavelength. It reveals that the photocycloreversion reaction heterogeneously took place in the shell of the diarylethene polymers upon irradiation at longer wavelength to be enhanced in proximity to the gold nanoparticles. The promotion of the photoreaction is due to the plasmonic enhancement effect both in the vicinity and in the gap of the gold nanoparticles.

1. Introduction

Plasmonic nanoparticles, especially gold and silver nanoparticles, have been utilized in wide variety of applications including coloring agent of glass artifacts and chemical sensors because of their brilliant colors. Meanwhile, a number of researchers have investigated their attractive electromagnetic properties [1–14]. The nanoparticles whose diameter is less than or comparable to the light wavelength generate electric field localized significantly in the vicinity of the particles, which is derived from resonance between the collective oscillation of conduction electrons and the incident light known as localized surface plasmon resonance (LSPR). The locally enhanced electric field affects the optical properties of molecules in proximity to the nanoparticle surface. Anomalous optical phenomena near the nanoparticles such as surface enhanced Raman scattering (SERS) [5,6], enhanced emission [7–9], energy transfer [10], photocurrent generation [11,12], and multiphoton excitation [13,14] have already been observed. Because of the amplified and confined electric field, the plasmonic nanoparticles are considered to be useful for efficient use of light whose wavelength corresponds to the LSPR band. However, although the enhancement effect on photophysical processes such as Raman scattering and fluorescence has been reported, there are less experimental studies focusing on the photochemical phenomena.

In order to demonstrate the efficient photoreaction field of the photochemical reaction, we have investigated the enhancement effect on the photochemical reaction by the nanoparticles and dependence of the reaction condition. The intended photoreactive molecule has to be lied on the surface of the particles in order to evaluate the plasmonic interaction between the nanoparticles and the photoreactive molecule. There are several experimental approaches that place the photoreactive molecule in proximity to the metal nanoparticles. One of such approaches has spread the intended molecules on the metal nanoparticles attached to a substrate or has coated the particles with the molecules dissolved in a polymer matrix [13,14]. Although it is easy to fabricate the complex of the nanoparticles and the photoreactive molecules, the photoreactive molecules are required putting some distance from the metal nanoparticle to observe the interaction by the plasmonic enhancement effect. One of ideal methods is a core–shell structure of metal nanoparticles and the intended molecules [15–19]. In the structure, the photoreactive molecules are located only near the particle and the distance from the surface can be controlled by changing the length of spacer moiety. Recently, we have synthesized and characterized gold nanoparticle covered with chain length-controlled photochromic diarylethene polymers (Au-poly(DE)) [20,21] as shown in Scheme 1 whose spectral changes upon photoirradiation could be easily traced in a solution and in the solid state because of the existence of a number of photoreactive chromophores around the gold core. Since Au-poly(DE) has the ideal core–shell structure consisting of the diarylethene polymer

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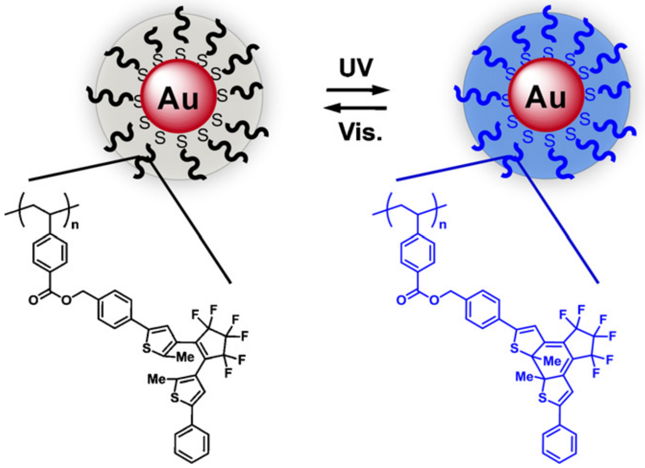

Scheme 1. Schematic illustration of photochromism of Au-poly(DE).

shell around the core particle, Au-poly(DE) is versatile to evaluate the enhancement effect around the gold nanoparticle.

In this paper, we have investigated the photochromic reactivities of Au-poly(DE) in the solid state to evaluate the plasmonic enhancement on the photochromic reaction. The photocyclization reaction of the diarylethene chromophore upon UV irradiation was not influenced in the vicinity of the particle, while the photocycloreversion reactivity upon exposure to visible light was strongly affected depending on the irradiation wavelength. It was found that there are two enhancement effects on the photocycloreversion reaction in the vicinity and in the gap of the gold nanoparticles in the solid state.

2. Experimental

2.1. Measurements

The absorption spectra were measured by a JASCO V-630 spectrophotometer. Photoirradiation was carried out using a 200 W mercury-xenon lamp (Moritex MUV-202) or a 100 W xenon lamp (Asahi Spectra LAX-Cute) as a light source. Monochromic light was obtained by passing the light through a monochromator (JASCO CT-10) and glass filters. The sample of Au-poly(DE) for photochromic reactions on the quartz glass was fabricated by casting a toluene solution of Au-poly(DE) ([Au-poly(DE)] = ca. 1 g $\mathrm{dm^{-3}}$) on the quartz glass. The transmission electron microscope (TEM) images were performed on a Hitachi H-7000 at 75 kV. The TEM sample was prepared by dropping a toluene solution of Au-poly(DE) ([Au-poly(DE)] = ca. 0.1 g $\mathrm{dm^{-3}}$) on a carbon-coated copper grid and removing the excess solution by a filter paper to dry under air. The atomic force microscope (AFM) images were obtained using a Digital Instruments NanoScope IIIa scanning probe microscope in the tapping mode with a silicon cantilever (OLYMPUS OMCL-AC240TS-C2) with a normal spring constant of 2 $\mathrm{N\,m^{-1}}$ and a resonant frequency of 70 kHz. The AFM sample was prepared by the method similar to the sample on the quartz glass described above.

2.2. Synthesis and characterization of Au-poly(DE)

Poly(DE) and Au-poly(DE) used were prepared and characterized by the same methods described in our previous papers [20–22]. Chain length-controlled poly(DE) was synthesized by a reversible addition–fragmentation chain transfer (RAFT) radical polymerization of a styrene bearing a diarylethene chromophore (DE) using 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) and 1-phenylethyl dithiobenzoate (PEDB) as an initiator and a RAFT agent, respectively, in toluene for 60 h at 100 °C ([DE] = 2.9 mol $\mathrm{dm^{-3}}$, [ATMP] = 1.0×10^{-3} mol $\mathrm{dm^{-3}}$, [PEDB] = 0.045 mol $\mathrm{dm^{-3}}$). Subsequently, the dithiobenzoate-end group in the polymer was reduced to thiol-end group by sodium borohydride in tetrahydrofuran (THF) and water. The degree of polymerization (n) of poly(DE) was determined by ^{1}H NMR spectroscopy and gel-permeation chromatography (GPC). Au-poly(DE) was synthesized using a seeding growth method, followed by a ligand exchange reaction. Mean diameter (d) of the gold core was determined from the TEM image using the image analysis program package ImageJ (http://rsb.info.nih.gov/ij/index.html).

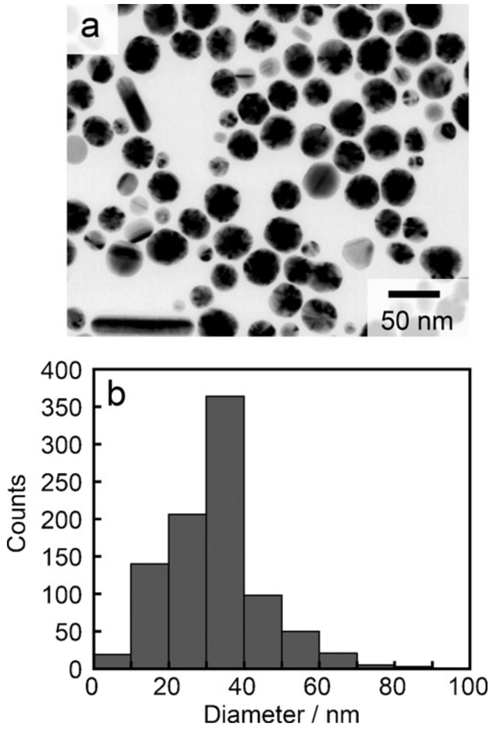

Fig. 1. (a) TEM image and (b) core size histogram of Au-poly(DE) (d = 32 nm, n = 48).

3. Results and discussion

3.1. Synthesis and characterization of Au-poly(DE)

Poly(DE) as the covering agent of the gold nanoparticle was synthesized by the RAFT radical polymerization, which can control molecular weight and polydispersity of the polymers and introduce a dithiobenzoate group at the ω-end. Poly(DE) bearing the dithiobenzoate group can be transformed to the thiol group as the end group by reductive reaction [22,23]. The degree of polymerization (n) and polydispersity ($M_\mathrm{w}/M_\mathrm{n}$) of the resulting poly(DE) were determined to be 48 and 1.06, respectively. The narrow polydispersity of the polymer indicates that the RAFT radical polymerization was successfully performed to obtain chain-length controlled poly(DE) (n = 48).

Au-poly(DE) was prepared by the seeding growth method, followed by the ligand exchange reaction using poly(DE) bearing the thiol-end group according to our previous paper [21]. TEM image and core size histogram of Au-poly(DE) were shown in Fig. 1. Mean diameter (d) and relative standard deviation of the core particle were determined to be 32 nm and 40%, respectively. Although some of rod-like clusters exist in the TEM image, Au-poly(DE) (d = 32 nm, n = 48) is basically dispersed individually on the copper grid.

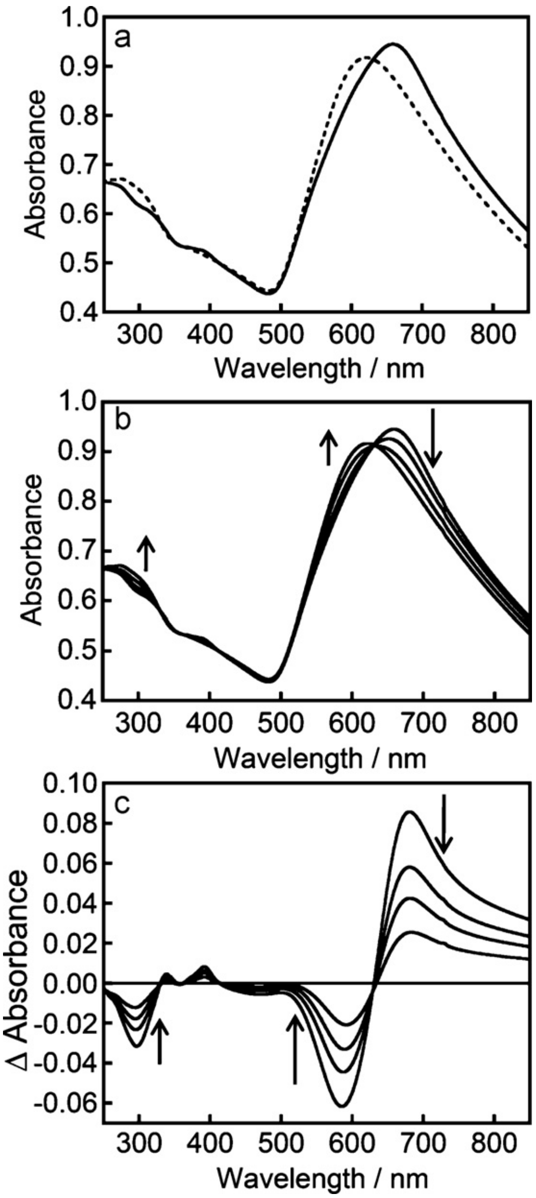

Fig. 2. (a) Absorption spectra of Au-poly(DE) on the quartz glass before (broken line) and after (solid line) irradiation at 313 nm and (b) absorption spectral changes and (c) difference spectral changes of Au-poly(DE) on the quartz glass upon irradiation at 500 nm.

3.2. *Photochromic reaction of Au-poly(DE) in the solid state*

The glass substrate of Au-poly(DE) was fabricated by casting a toluene solution of Au-poly(DE) on the quartz glass. Fig. 2a shows absorption spectral changes of Au-poly(DE) on the quartz glass substrate upon irradiation at 313 nm. The strong LSPR band of Au-poly(DE) on the quartz glass before photoirradiation is located at 620 nm, which is derived from the interparticle distance closer than that dispersed in a solution [21]. The LSPR band was shifted to the longer wavelength at 659 nm upon irradiation with UV light. The shift in the LSPR band is ascribed to the refractive index changes in the diarylethene polymer shell [21]. Absorption spectral changes and difference spectral changes upon irradiation at 500 nm were shown in Fig. 2b and c. The difference spectra were obtained by subtracting the absorption spectrum of the initial Au-poly(DE) having the open-ring form from each absorption spectrum in Fig. 2b. The initial difference spectrum before visible light irradiation corresponds to that in the photostationary state (PSS) upon UV irradiation. As we reported in our previous paper [21], the difference spectrum has a spectral dip in visible region in PSS, which is due to the shift of the LSPR band according to the photochromic reaction. Upon visible light irradiation, the closed-ring form of the diarylethene chromophore returned to the open-ring form and the LSPR band reverted to the original position. The reversible change in the LSPR band can be repeated at least several times upon alternating irradiation with UV and visible light. It is worth mentioning that there are the isosbestic points at 320 and 630 nm during the cycloreversion reaction of poly(DE). The isosbestic points were observed during both the photocyclization and photocycloreversion reactions. In other words, the difference spectrum vertically increased or decreased keeping the spectral shape upon irradiation at 313 and 550 nm. These results indicate that the LSPR band is shifted in proportion to the spectral change of the diarylethene chromophore.

3.3. *Wavelength dependence on the photocycloreversion reaction*

The absorption spectral changes and difference spectral changes upon irradiation at 600, 650, and 700 nm are shown in Fig. 3. It is noticed that the spectral changes obviously differ from each other upon exposure to visible light. The isosbestic point was observed in the spectral changes upon irradiation at 600 nm, whereas no longer was observed upon irradiation at 650 and 700 nm. In addition, the absorption maximum in the difference spectra upon irradiation at 700 nm was significantly shifted to shorter wavelength side along with the photocycloreversion reaction. The disappearance of the isosbestic point and the difference in the spectral shape changes are more pronounced upon irradiation at longer wavelength as can be seen in Fig. 3, which clearly means the wavelength dependence of the photocycloreversion reaction of poly(DE) around the gold nanoparticle in the solid state.

The difference in the spectral changes can be explained as follows. As mentioned above, the isosbestic point upon irradiation at 500 nm indicates that the spectral change of diarylethene chromophore and the shift in the LSPR band proportionally took place along with the photoreaction. Therefore, the photocycloreversion reaction upon irradiation at 500 nm is considered to take place homogeneously in the poly(DE) shell. In contrast, the spectral changes upon irradiation at 650 and 700 nm have no isosbestic point, which means that the heterogeneous cycloreversion reaction in the poly(DE) shell may imply the promoted photochromic reaction near the gold nanoparticle.

3.4. *Analysis of enhancement of the photocycloreversion reaction*

In order to evaluate whether the photocycloreversion reaction is enhanced upon irradiation at various wavelengths, the decrease of absolute Δabsorbance at the negative absorption maximum wavelength at 296 nm upon irradiation with visible light was plotted against that at 585 nm. The relationship is shown in Fig. 4. The Δabsorbance in the UV region is derived from the content of the closed-ring form of the diarylethene chromophore in the poly(DE) shell ([Closed-ring form]). Therefore, the decrease in the ratio of [Closed-ring form] to that in the PSS upon irradiation at 313 nm ([Closed-ring form]$_{\mathrm{PSS}}$) corresponds to the proportion of the closed-ring form that underwent the photocycloreversion reaction in the poly(DE) shell. However, Δabsorbance in the visible region can be regarded as the LSPR band change along with the photochromic reaction of the poly(DE) shell because the absorption of the diarylethene closed-ring form in the visible region estimated from the peak intensity in the UV region is quite small in comparison with the spectral dip corresponding to the LSPR band shift. It means that the decrease of absolute Δabsorbance at 585 nm is regarded as the photocycloreversion reaction in proximity to

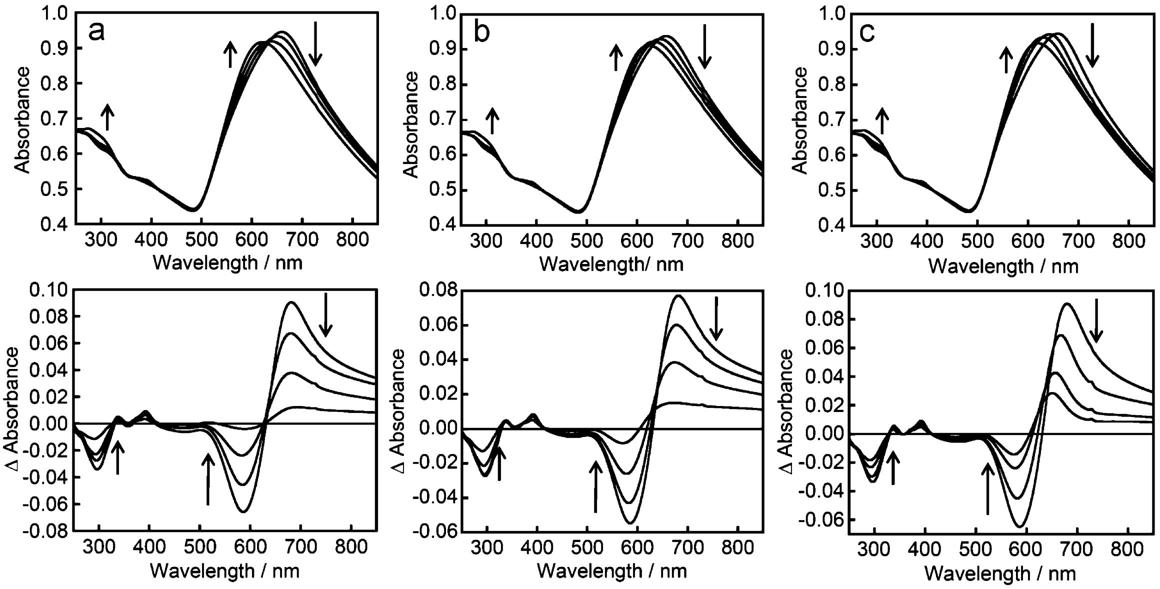

Fig. 3. Absorption spectral changes (upper) and difference spectral changes (lower) of Au-poly(DE) on the quartz glass upon irradiation at (a) 600 nm, (b) 650 nm, and (c) 700 nm.

the gold nanoparticle. Approximately–linear relationship between the horizontal and the vertical axes observed upon irradiation at 500 nm indicates the homogeneous photocycloreversion reaction in the poly(DE) shell as well as that upon irradiation at 313 nm. The result can be supported from the existence of the isosbestic point in Fig. 2b and c. Meanwhile, the relationship upon irradiation at 700 nm describes a curve, which indicates that the LSPR band was shifted faster than that derived from the homogeneous photocycloreversion reaction. This result clearly implies that the diarylethene chromophore reacted from the vicinity of the gold nanoparticles. In other words, the photocycloreversion reaction in the neighborhood of the particles underwent more efficiently than that far from the particles.

Similar plots upon irradiation at 550, 600, and 650 nm are shown in Fig. 5. The three plots also showed curves. The slopes at the initial stage of the photocycloreversion reaction upon irradiation at 550, 600, and 650 nm were estimated to be ca. 3, 5, and 14, respectively. The larger slope corresponding to the enhancement effect of the photocycloreversion reaction near the particle was observed at the longer wavelength. Furthermore, the trend of the curvature is in good accordance with that of the disappearance of the isosbestic point shown in Fig. 3. It reveals that the inhomogeneous photocycloreversion reaction is related to the promotion of the photocycloreversion reaction in proximity to gold nanoparticle. Interestingly, the curve of the plot upon irradiation at 650 nm is comparable to that at 700 nm, while large difference in the spectral changes was observed as shown in Fig. 3b and c. This means that the photochromic reaction upon irradiation at 700 nm includes more inhomogeneous reaction segment than that at shorter irradiation wavelength. The LSPR mode for closely approached gold nanoparticles appears from visible red to near infrared (NIR) region

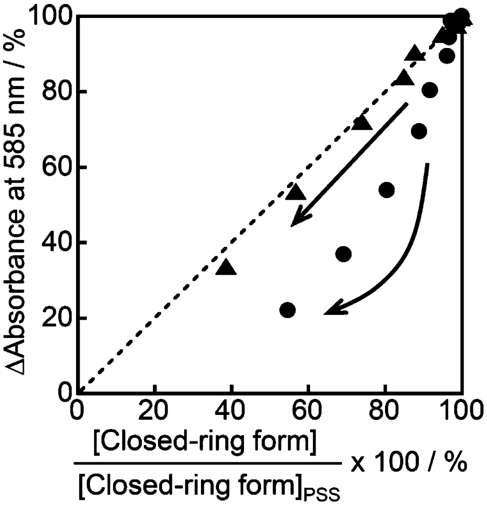

Fig. 4. Relationship between the rate of the closed-ring form of diarylethene chromophore in the poly(DE) shell ([Closed-ring form]) to that in the PSS upon irradiation at 313 nm ([Closed-ring form]$_{PSS}$) and Δabsorbance at 585 nm in the difference spectral changes of Au-poly(DE) in the solid state upon irradiation at 500 (solid triangle) and 700 nm (solid circle). The Δabsorbance at 585 nm in the PSS is normalized to 100%. Standard deviations are within 2% and 4% in the direction of the vertical and horizontal axes, respectively.

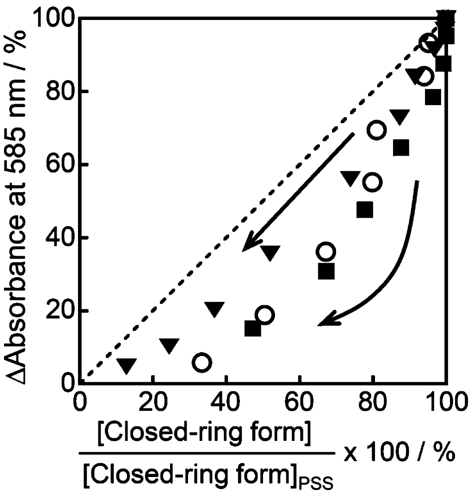

Fig. 5. Relationship between the rate of the closed-ring form of diarylethene chromophore in the poly(DE) shell ([Closed-ring form]) to that in the PSS upon irradiation at 313 nm ([Closed-ring form]$_{PSS}$) and Δabsorbance at 585 nm in the difference spectral changes of Au-poly(DE) in the solid state upon irradiation at 550 (solid inverted triangle), 600 (open circle), and 650 nm (solid square). The Δabsorbance at 585 nm in the PSS is normalized to 100%. Standard deviations are within 2% and 4% in the direction of the vertical and horizontal axes, respectively.

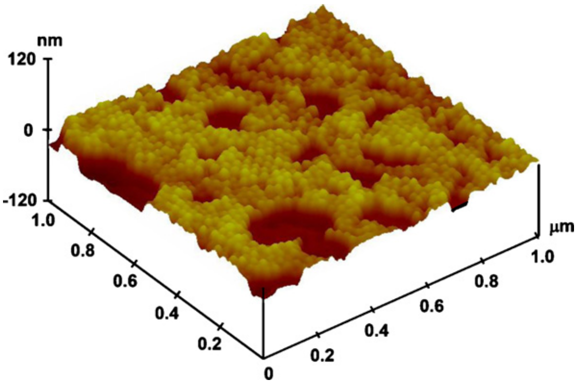

Fig. 6. Stereoscopic view of AFM image of Au-poly(DE) on the quartz glass.

depending on the interparticle distance [24,25], and the gap mode-induced photoexcitation can be achieved upon irradiation at longer wavelength side (∼800 nm) [13,14]. In fact, the interparticle distance of Au-poly(DE) on the quartz glass is close enough to be affected by the gap mode effect as shown in Fig. 6. Taking into account these insights, the peculiar spectral behavior upon irradiation at 700 nm is considered to be due to the gap-mode excitation of the diarylethene chromophore.

4. Conclusion

We prepared Au-poly(DE) casted onto the quartz glass substrate and investigated the photocycloreversion reactivities of the diarylethene chromophore around the gold nanoparticle upon irradiation at various wavelengths. Although the closed-ring form of the chromophore reverted to the open-ring form upon each irradiation condition, the behavior of the spectral changes showed significant wavelength dependence. It was found that the dependence is closely related to the enhanced photocycloreversion reaction of the diarylethene chromophore in the vicinity of the gold nanoparticle upon irradiation at longer wavelength. Upon irradiation at 700 nm, the spectral behavior implies the gap-mode enhancement of the photochromic reaction.

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