Photo- and Electrochromic Switching of Diarylethene–Gold Nanoparticle Network on Interdigitated Electrodes

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Conductance switching of a diarylethene–gold nanoparticles network was demonstrated by cyclization reaction induced with chemical oxidation and cycloreversion reaction with photoirradiation. The electrochromic reaction enables the cyclization reaction of the diarylethene whose photocyclization is strongly quenched by gold nanoparticles.

Photochromic diarylethenes can be photochemical molecular switches in molecular electronics because the color change originates from the reversible change of π-conjugation under photoirradiation.[1] Although several reports have appeared in the literature concerning properties of diarylethenes with respect to molecular electronics,[2] quenching of the photoexcited state by metal surface and nanoparticles is a fatal drawback.[3] For the realization of practical molecular switching devices, the switching should proceed in both directions smoothly.

Electrochromic reaction of diarylethenes could be a strong candidate for an alternative external stimulus because the isomerization is induced by electrochemical oxidation or chemical oxidation whose mechanism is different from the photoisomerization.[4]

In this letter, we report conductance switching of a diarylethene–gold nanoparticle network system using photo- and electrochromic reactions on interdigitated electrodes as illustrated in Figure 1. As external stimuli, photoirradiation and chemical oxidation by $FeCl_3$ were used.

As a diarylethene linker that shows both photo- and electrochromic reactivities, we chose 1,2-bis[5-(5-sulfanyl-2-thienyl)-2-methyl-3-thienyl]perfluorocyclopentene (**1**) (Figure 1). According to the literature on dynamics,[5] theoretical calculation,[6] and spectroscopy,[7] the cyclization reaction of the thiophene-substituted dithienylethene is strongly quenched when placed on gold nanoparticles and surfaces. Because of this drawback, only one-way photoswitching properties have been reported for single-molecular devices.[8] This might be overcome by an electrochromic oxidative cyclization that was first reported for this type of compound by Peters and Branda.[9]

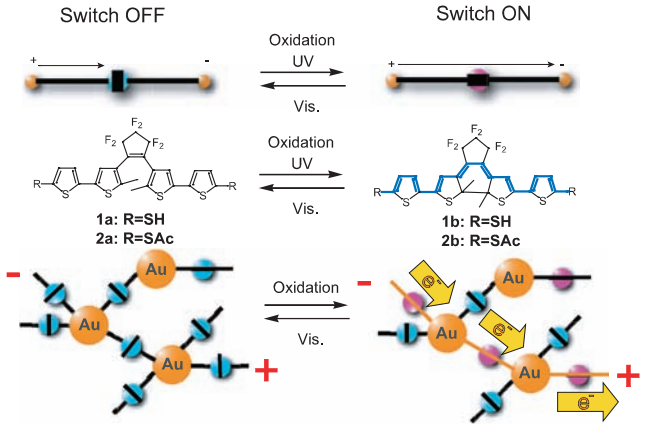

Figure 1. Molecular structure of the diarylethenes and schematic illustration of the gold nanoparticle network.

The synthetic scheme of ligand **1** is described in Scheme S1.[10,11] We used a trimethylsilylethyl[12] for the protection of the thiol group. Because diarylethene dithiol **1** is apt to form polymer by-products by the formation of S–S bonds, the characterization of the ligand was performed on acetyl-protected diarylethene **2**.

The photochromic reactivity of ligand **2** was confirmed by the absorption spectral change. As in a previous report, this compound showed reversible photochromic reaction under photoirradiation (Figure S1[10]). According to the absorption spectra of compound **2**, the conversion to the closed-ring isomer in the photostationary state was estimated to be 98% under irradiation with 365-nm light. The high conversion ratio suggests that the quantum yield of the cyclization reaction is much larger than that of the cycloreversion reaction.[13]

The oxidative cyclization of ligand **2a** was investigated by cyclic voltammetry (CV). Figure S2a[10] shows the voltammogram of ligand **2** for the first two cycles. When **2a** is oxidized at $V > +1.0$ V (vs. Ag/Ag^+), a reduction peak at $+0.54$ V is observed. After two cycles, a reversible redox peak was observed at around $+0.6$ V and the current value above $+0.95$ V decreased. This new redox peak corresponds to that of UV irradiated colored sample (Figure S2b[10]), suggesting the formation of the closed-ring isomer by oxidation.

Diarylethene–gold nanoparticle network Au–**1a** was prepared by ligand exchange. When the gold nanoparticle solution was mixed with the diarylethene solution, the solution turned from burgundy red to blueish purple. This is due to the interplasmon coupling originating from the formation of network structure. Figure 2a shows the transmission electron micrograph (TEM) image of the Au–**1a** network. As shown in the inset, spherical nanostructure with a diameter around 1.5 μm was observed. The expanded image of structure shows that the sphere consists of the multilayered network structure of gold nanoparticles.

The prepared Au–**1a** network was placed on a interdigitated gold electrode (NTT, gap width: 5 μm). Figure 2b shows the scanning electron micrograph (SEM) image of the electrode. The black region is the gap and the white region is the gold electrode. Several spheres with a diameter around ca. 1 μm were observed between the gap. The EDX elemental analysis of the

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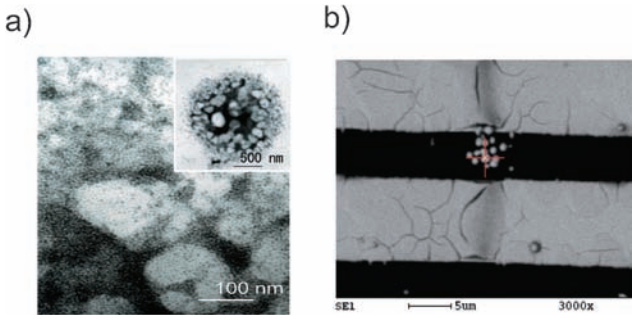

Figure 2. a) TEM images of the Au–**1a** network. The inset is an overall view of the structure. b) SEM image of fabricated electrode.

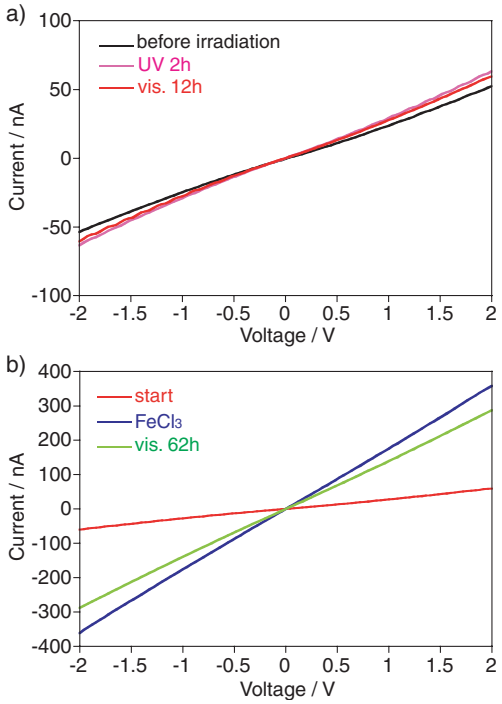

Figure 3. *I*–*V* curves of the Au–**1a** network on the interdigitated electrode. All measurements were performed under vacuum. a) *I*–*V* curves after photoirradiation. b) Change of *I*–*V* curve by chemical oxidation with $FeCl_3$ acetone solution and photoirradiation.

spheres showed that the content of gold was 46 wt %, which is clearly larger than the empty gap (9.9 wt %). We suppose that the nanostructure consists of gold nanoparticles. The color change of the electrode also supports the formation of the network structure on the interdigitated electrodes (Figure S3[10]).

Figure 3a shows the *I*–*V* curves of the fabricated interdigitated electrode under irradiation with UV ($320 < \lambda < 380$ nm) under vacuum. The conductance of the Au–**1a** network hardly changed under irradiation with UV for 2 h. This result shows the strong quenching effect of the cyclization reaction of the thienyl-substituted dithienylethene by gold nanoparticles, which was not severe for phenyl-substituted dithienylethene,[14] as suggested in other reports.[6,7]

The conductive switching was then performed by electrochromic reaction. The fabricated electrode was soaked in 12 mM $FeCl_3$ in acetone for 1 min and moved to the vacuum chamber again. Figure 3b shows the conductance change of the Au–**1a** network. The conductance was increased about 5-fold. The increase of the conductance can be explained by the electrochromic reaction from OFF (the open-ring isomer) to ON (the closed-ring isomer).

In order to verify the increase in conductance, the cycloreversion reaction was carried out by irradiation with visible ($\lambda > 510$ nm) light. As shown in the green *I*–*V* curve in Figure 3b, the conductance of the network slowly decreased under irradiation with visible light for 62 h. This switching behavior suggests that the closed-ring isomer in the network showed cycloreversion by photoexcitation. The slow reaction rate is due to the low quantum yield of the reaction, which was reported previously.[14]

In conclusion, we have demonstrated photo- and electrochromic conductance switching of a diarylethene–gold nanoparticle network. Electrochromism of the diarylethene ligand overcame the quenching effect of the photoexcited state on gold nanoparticles. This concept will realize a new switching behavior in molecular electronics with diarylethene.

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