Photoswitching of conductance of diarylethene-Au nanoparticle network†

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A network composed of gold nanoparticles covered with diarylethene dithiophenols was prepared on an interdigitated nanogapped gold electrode to show the reversible photoswitching of the conductance due to the photochromism of the diarylethene molecules induced by UV and visible light.

"Molecular electronics" is a rapidly expanding field in nanoscience and nanotechnology. Molecular electronics can be defined narrowly as the study of electrical and electronic processes by accessing the individual molecules with electrodes and exploiting the molecular structure to control the flow of electrical signals through them.[1]

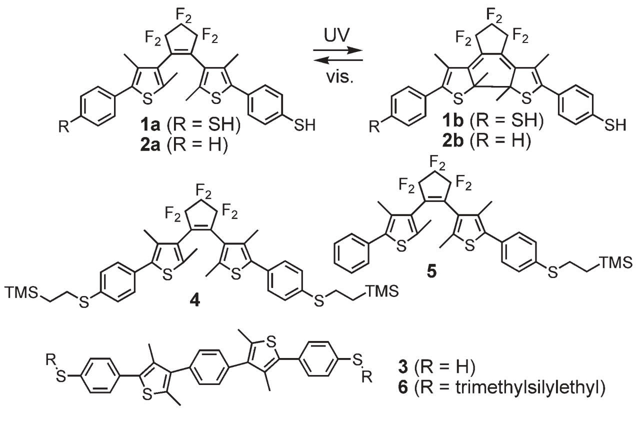
Recently, we have been studying the photoswitching of the intramolecular magnetic exchange interaction by using a diarylethene photochromic spin coupler carrying a nitroxide radical at each end.[2] The photoisomerization of the π-conjugated spin coupler gives rise to a switching of the exchange interaction by more than 150-fold. The spins are localized in the nitroxide moiety in these studies, and so the exchange interaction between spins can be regarded as an analogue of the conductance between electrodes. Both the exchange interaction[3] and the tunneling current[4] show an inverse exponential dependence on the distance.

Although there are increasing numbers of reports dealing with the conductance of single molecules, studies on photoswitchable molecules are very rare.[5] Besides, studies on the conductance of networks prepared with organic molecules and Au nanoparticles on interdigitated nanogapped electrodes are attracting interest because of the relatively easy preparation and the applicability to the small number of molecules.[6] In this paper, the photoswitching of the conductance of a diarylethene-Au nanoparticle network is reported. We have already reported the photochromic reaction of gold nanoparticles covered with diarylethenes with mercaptopentyl groups[7] and Feringa and co-workers have recently reported that a diarylethene connected to Au surface without alkyl spacers also undergoes the photochromic reaction.[8] Although the excited state of organic molecules on noble metal surfaces is considered to be easily quenched by the surface plasmon resonance, the diarylethene on Au nanoparticles showed reversible photochromism. This is attributed to the fast photoreaction of diarylethenes in comparison with the quenching by the Au metal surface.

Considering that conjugated molecules have a much better conductance than non-conjugated molecules,[9] sulfur atom should be attached directly to the π-conjugated system despite the anticipated quenching of the excited state. Thus, diarylethene dithiophenol **1a** was designed and synthesized (Scheme 1) (for details see ESI†). The two introduced thiophenol units bridge the Au nanoparticles and create a conducting path between electrodes (Fig. 1). Au nanoparticles covered with monothiophenol **2a** were synthesized to see the effect of the direct attachment on the photoreactivity. During the synthetic procedure, trimethylsilylethyl protecting groups were found to work effectively for the thiophenol moiety (compounds **4–6** in Scheme 1).[10] Although the thiophenols **1a** and **2a** were sufficiently characterized, they were easily oxidized to form disulfides, so that the preparation of the diarylethene-covered gold nanoparticles was carried out immediately after the deprotection. For reference studies, non-photoreactive dithiophenol **3** was also prepared.

Dithiophenol **1a** and monothiophenol **2a** underwent reversible photochromic reactions in ethyl acetate upon alternate irradiation with 313 and 578 nm light. The open-ring isomers **1a** and **2a** showed absorption maxima at 287 and 278 nm, respectively, and had no absorption in the visible region, while the closed-ring isomers **1b** and **2b** both showed absorption at 577 nm (see ESI†).

Preparation of the **Au-1a** nanoparticle network was carried out according to the procedure of Tamada and co-workers[11] Au nanoparticles protected by tetraoctylammonium bromide (TOAB) were first prepared and then the dithiophenol **1a** was reacted with the TOAB-protected Au nanoparticles. In this method, the



Scheme 1 Photochromic reactions of diarylethenes **1** and **2**. The structures of the precursors and the reference compounds are also shown.

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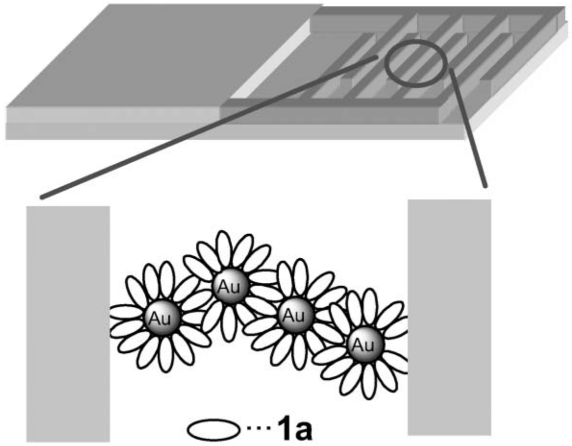

Fig. 1 Schematic drawing of the diarylethene-Au nanoparticle network on an interdigitated nanogapped Au electrode.

formation of the nanoparticles occurred before the reaction with the dithiol, so that the size and shape of the nanoparticles could be controlled.[12] The prepared **Au-1a** network was characterized by transmission electron microscopy (TEM) (Fig. 2). TEM images show clearly the formation of the network structure. The size of the nanoparticles was obtained as 3.6 ± 0.7 nm. The IR spectrum of the **Au-1a** network showed the characteristic peaks of **1a**, suggesting the incorporation of the diarylethene.

The **Au-1** network showed photochromism in the solid state (Fig. 3). The absorption spectra of the **Au-1** network was measured in KBr. The spectrum showed reversible changes along with the photochromism. From the difference spectra the absorption maximum of the closed-ring isomer **Au-1b** was determined to be 628 nm, which thus showed a large bathochromic shift compared with free **1b**, indicating the perturbation of the electronic structure of the closed-ring isomer **1b** by Au. The gold nanoparticles prepared from monothiophenol **2a** also showed photochromism though it was less reactive than the previously reported alkyl-containing analogue. The absorption maximum of **Au-2b** measured in ethyl acetate was 609 nm, which also showed a bathochromic shift on the Au surface.

The **Au-1a** nanoparticle network was prepared on the interdigitated nanogapped Au electrode (NTT-AT, 5 μm gap). The preparation of the network was performed on the electrode by mixing the TOAB-protected Au nanoparticles and a freshly prepared solution of **1a**. Scanning electron microscopy (SEM) measurement showed the formation of bridging between the electrodes (see ESI†).

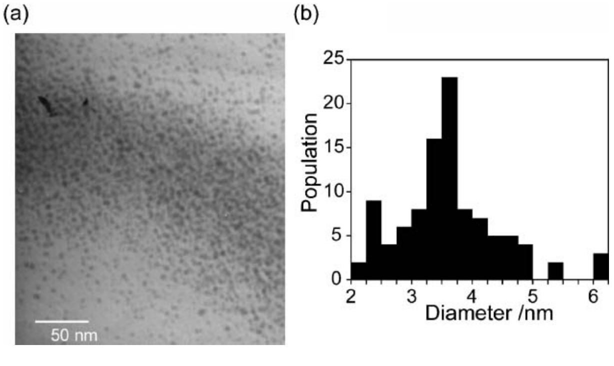

Fig. 2 (a) TEM image of the **Au-1a** network (100 kV, × 50000). (b) Histogram of the size of the nanoparticles in the **Au-1a** network.

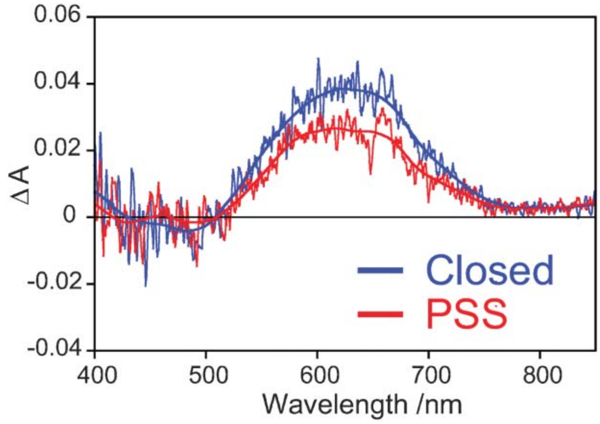

Fig. 3 Difference absorption spectra of the **Au-1** network prepared from the closed-ring isomer **1b**. The spectra were obtained by subtraction of the open-ring isomer spectrum which was measured after irradiation with 578 nm light. Measurement was performed in a KBr matrix. Closed: as prepared; PSS: after irradiation with 578 and then 313 nm light.

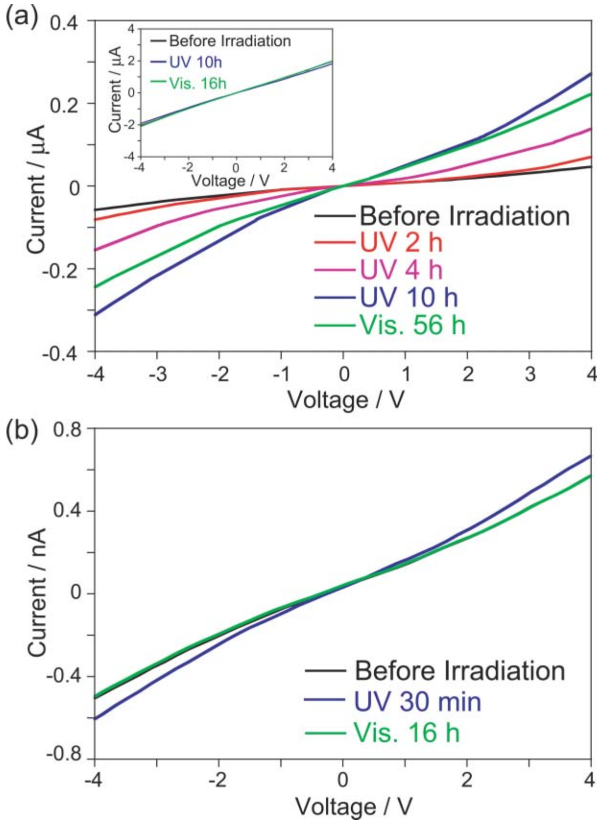

Fig. 4 (a) Change of the *I–V* curve of the **Au-1** network and (inset) the **Au-3** network on the interdigitated Au nanogapped electrode. UV light (290 nm < λ < 380 nm) and visible light (560 nm < λ) was used for the experiment. (b) The same measurement was performed with a shorter time of the UV irradiation. In this case, the conductance showed clear reversibility.

Conductance was measured during the alternate irradiation with UV and visible light (Fig. 4). Upon irradiation with UV light (290 nm $< \lambda <$ 380 nm), the conductance increased significantly, while the conductance decreased upon irradiation with visible light (560 nm $< \lambda$) (Fig. 4(a)). The **Au-3** network, prepared for reference, did not show any change upon photoirradiation (Fig. 4(a), inset). The photoreaction of the **Au-1a** nanoparticle network was very slow, especially for the ring-opening reaction due to the severe quenching, which is also observed in the **Au-2a** nanoparticles. When the UV irradiation was carried out for 10 h, the maximum ON/OFF ratio of the conductance was more than five-fold, but the conductance was not completely restored by visible irradiation. To check the reversibility, the same measurement was performed with 30 min of UV irradiation, which is shorter than in the previous experiment (Fig. 4(b)). In this case, the ON/OFF ratio was as small as 1.2-fold, but complete reversibility was observed. The absolute value of the conductance varied with the different setups because the network formed on the electrode varied with the different setups. However, the photochemical change of the conductance did not vary.

In conclusion, by preparing a diarylethene-Au nanoparticle network made of diarylethene dithiophenol, the photoswitching of conductance though the organic molecule has been achieved. By using narrower gapped electrodes, digital-type switching should be possible.

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