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Bio-inspired photoresponse of porphyrin-attached gold nanoparticles on a field-effect transistor ☆

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ABSTRACT

A bio-inspired photoresponse was engineered in porphyrin-attached Au nanoparticles (AuNPs) on a field-effect transistor (FET). The system mimics photosynthetic electron transfer, using porphyrin derivatives as photosensitizers and AuNPs as photoelectron counting devices. Porphyrin-protected AuNPs were immobilized onto the gate of an FET via the formation of self-assembled monolayers. Photoinduced electron transfer from the porphyrin led to single electron transfer at the Au nanoparticles, which was monitored via a changing gate voltage on the FET in the presence of organic electrolyte. The further attachment of other functional molecules to this system should enable various other potential functionalities. This article is part of a Special Issue entitled: Photosynthesis Research for Sustainability: Keys to Produce Clean Energy.

1. Introduction

Natural photosynthesis is a model energy conversion system that achieves excellent electron flow with high quantum yield [1,2]. The *Z*-scheme, a combined system of successive alternating energy-raising photon absorptions and energy-using electron transport processes, enables photosynthesis to effectively transfer electrons within a specific arrangement of proteins surrounding reaction center molecules. Photon sensing is an application of artificial photosynthesis processes. Charge-coupled devices (CCDs), which employ photo-diodes, are the most popular class of photon-sensing device. A drawback is their need of large, energy-consuming cooling systems. Conceivable future photo-detection applications include artificial retinas, which must be smaller and more sensitive than current devices.

The necessary improvements to current photon-sensing technology might be achievable by mimicking photosynthesis via specially arranged electron-transfer photosystems that use a specific type of artificial molecule: a molecular wire [3–9]. A molecular wire consists of a biophilic moiety and an electron storage moiety. Attempts to replicate photosystem I, a process in the *Z*-scheme of natural photosynthesis, have used molecular wires with Au nanoparticles. A molecular wire with a 1,4-naphthoquinone moiety, which replaces vitamin K_1 in the electron transfer pathway of photosystem I, has been developed. Each molecular wire is terminated with an Au nanoparticle, which should be smaller than 2 nm. Each nanoparticle requires sufficiently low capacitance to show single electron transfer (SET) [10–19]. A prototype of this photon counter was successfully demonstrated by our group with a specific image trace. However, SET at the Au nanoparticles was weakened in the aqueous solution conditions often required for practical photosystems [20]. The development of organic, rather than aqueous, electrolyte systems might aid the capacitance of Au nanoparticles for better SET.

In the present study, we developed a photo-detection system that combined a porphyrin derivative, AuNPs, and an FET with an Au gate (Fig. 1). First, porphyrin receives light energy and transfers an excited electron to benzyl bromide (BnBr, a sacrificial reagent). Next, the hole in the porphyrin is compensated via electron transfer from the AuNPs. Due to the SET at the AuNPs, a voltage change at the Au electrode can be observed as a photoresponse.

2. Materials and methods

2.1. Materials

All chemical reagents were from commercial sources and used without additional purification. FET chips, each with a gate coated with a

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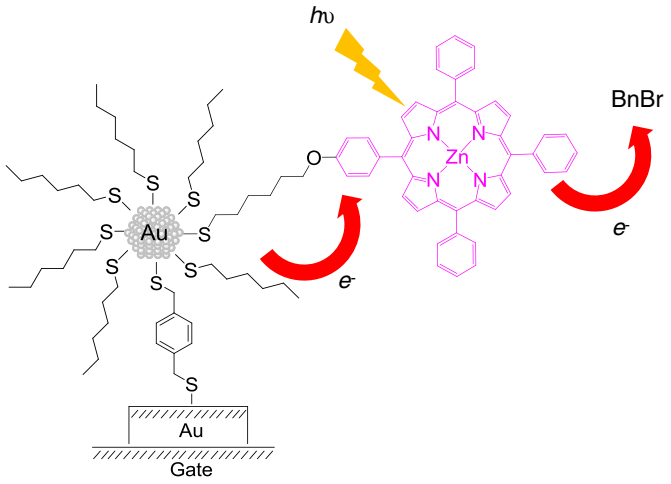

Fig. 1. Schematic of the photon counter.

thin Au layer, were developed specifically for this study. The effective area of the Au electrode on the gate was 16.7 × 16.7 μm^2.

2.2. Characterization

Elemental analysis of the products was measured on a Yanaco MT-6 C,H,N corder at the Elemental Analysis Center of the University of Tokyo, Tokyo, Japan. Field-emission transmission electron microscopy (FE-TEM) was conducted at 200 kV using a Hitachi HF-2000 instrument equipped with an AMT-CCD camera. AuNPs were prepared for TEM at room temperature by depositing CH_2Cl_2-dispersed particles on a carbon film supported by a copper grid. The size distribution of the nanoparticles was obtained by manually measuring particle diameters from the TEM images.

2.3. Synthesis of **2** ($Au_x(SC_6H_{13})_y(S(CH_2)_6O–ZnTPP)_z$)

AuNPs attached with porphyrin (**2**, $Au_x(SC_6H_{13})_y(S(CH_2)_6O–ZnTPP)_z$) (TPP: tetraphenylporphyrin) were prepared by the modification of a reported method [3]. Initially, 1-hexanethiol-protected AuNPs ($Au_x(SC_6H_{13})_y$) were prepared with reference to the Brust method [21]. Porphyrin **1** was synthesized according to the literature [22–24]. A thiol exchange reaction on the nanoparticle surface was then accomplished as follows [25]: to the dispersion of AuNPs (92 mg) in CH_2Cl_2 (5 mL) was added **1** (106.2 mg); the mixture was then stirred for 6.5 h under N_2 at room temperature. Next, **1** (97.7 mg) in CH_2Cl_2 (2 mL) was added to the mixture. After overnight stirring, the mixture was concentrated in vacuo until ca. 3.5 mL. Acetone (30 mL) was added to the CH_2Cl_2 dispersion, which was then held without stirring at 253 K overnight to allow precipitation. The precipitate was collected and dispersed in CH_2Cl_2 (4 mL). Acetone (30 mL) was added, and the CH_2Cl_2 solution was similarly precipitated overnight at 253 K. The concentration and precipitation process was repeated once more to afford **2** (29.1 mg). The average particle size was estimated to be 1.9 ± 0.2 nm from TEM images. Elemental analysis found C: 13.81%, H: 1.72%, and N: 0.51%.

2.4. Fabrication of porphyrin-AuNP-attached FET **3**

A thin Au layer on the gate of an FET was treated with an ethanol solution of 1,4-benzenedimethanethiol (10 mM) for 12 h at room temperature, washed with ethanol, and dried under flowing nitrogen. The FET gate was subsequently immersed in a solution of AuNPs **2** in 2-propanol (1 mM) for 14 d, washed with 2-propanol, and dried under flowing nitrogen to give the desired modified FET **3** (Fig. 2(a)). A modified Au electrode with directly attached porphyrin **2** (with no AuNPs) was similarly prepared as a control (Fig. 2(b)): the FET gate was immersed in a solution of porphyrin **1** in 2-propanol (1 mM) for 3 d to give FET **4**.

2.5. Photoresponse measurement

Photo-detection measurements were performed using a 100 W halogen lamp (Mitutoyo Megalight 100) and a parameter analyzer (Agilent HP4142B). Light from the lamp was monochromated using a monochromator and focused on the area of the Au electrode using an optical lens and a fiber via a microscope system. The parameter analyzer was used to detect the gate voltage change through a voltage follower circuit, which we originally developed to increase the sensitivity of photo-detection [26,27]. All measurements were taken at room temperature. The electrolyte used during photo-detection was 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) with 2 mM benzyl bromide (BnBr) in acetonitrile.

Potential was applied to the gate of the FET with the reference electrode used for the voltage supplier. The drain–source current I_d versus the voltage of the reference electrode was measured; its profile (i.e., an *I*–*V* curve) was used to calculate the voltage change of the photoresponse. The photoresponse of the modified gate was measured by plotting I_d versus time (i.e., an I_d–*t* plot). The obtained difference of I_d was calculated as the difference of the gate voltage compared with the *I*–*V* curve measured before irradiation.

3. Results and discussion

AuNPs **2** attached with porphyrin **1** were prepared via a thiol exchange reaction (Fig. 2). TEM showed the AuNPs **2** to be 1.9 ± 0.2 nm after the three-time repeated precipitation with acetone and dichloromethane (Fig. 3). These nanoparticles each contained 225 Au atoms, which is reported to be a significant amount [28]. Elemental analysis showed C: 13.81%, H: 1.72%, and N: 0.51%. The particle size and elemental analyses indicate that the composition of the AuNPs **2** was $Au_{225}(SC_6H_{13})_{61}(S(CH_2)_6O–ZnTPP)_5$ (C: 13.41%, H: 1.80%, and N: 0.51%). These results suggest that an average of five molecules of porphyrin **1** were attached to the surface of each nanoparticle.

AuNPs **2** were immobilized onto the Au gate electrode through the formation of self-assembled monolayers (SAMs). The Au electrode was immersed in 1,4-benzenedimethanethiol in ethanol (10 mM), which acted as an anchor to attach the particles to the electrode. The modified Au electrode was subsequently immersed in a dispersion of AuNPs **2** in 2-propanol (1 mM), which gave the AuNP-modified Au electrode **3** on the gate of the FET. A similarly modified Au gate electrode, which had porphyrin **1** directly attached without AuNPs, was fabricated as a control FET **4**.

The I_d–*V* characteristic curve of the modified electrode **3** was measured using the parameter analyzer (Fig. S1 in the Supplementary data). An Ag/AgCl reference electrode was used to supply voltage to the gate of the FET. The gate voltage was the same as that applied to the reference electrode, in accordance with the voltage follower circuit mechanism we had previously developed [26]. The I_d–*V* curve was used for calculation of the photoresponse of the gate voltage change.

The photoresponse of the FET **3** was induced under irradiation with monochromatic 430 nm light. The wavelength of the irradiation light was determined in reference to the Fig. S2 in the Supplementary data. The photoresponse was measured at the different reference voltages through the change of I_d (Fig. 4(a)–(c)). I_d changed positively upon irradiation in all cases. The observed changes of I_d were converted into equivalent changes of gate voltage using the previously measured I_d–*V* curve (Fig. S1 in the Supplementary data). The calculated differences of voltage corresponding to (a)–(c) in Fig. 4 were 7, 6, and 6 mV, respectively. The similar values of the voltage changes show that they were due to the photoresponses of the gate on the FET **3**.

Fig. 4(d) shows the I_d photoresponse of the modified gate on FET **4** that lacked AuNPs. I_d changed positively upon irradiation, but the

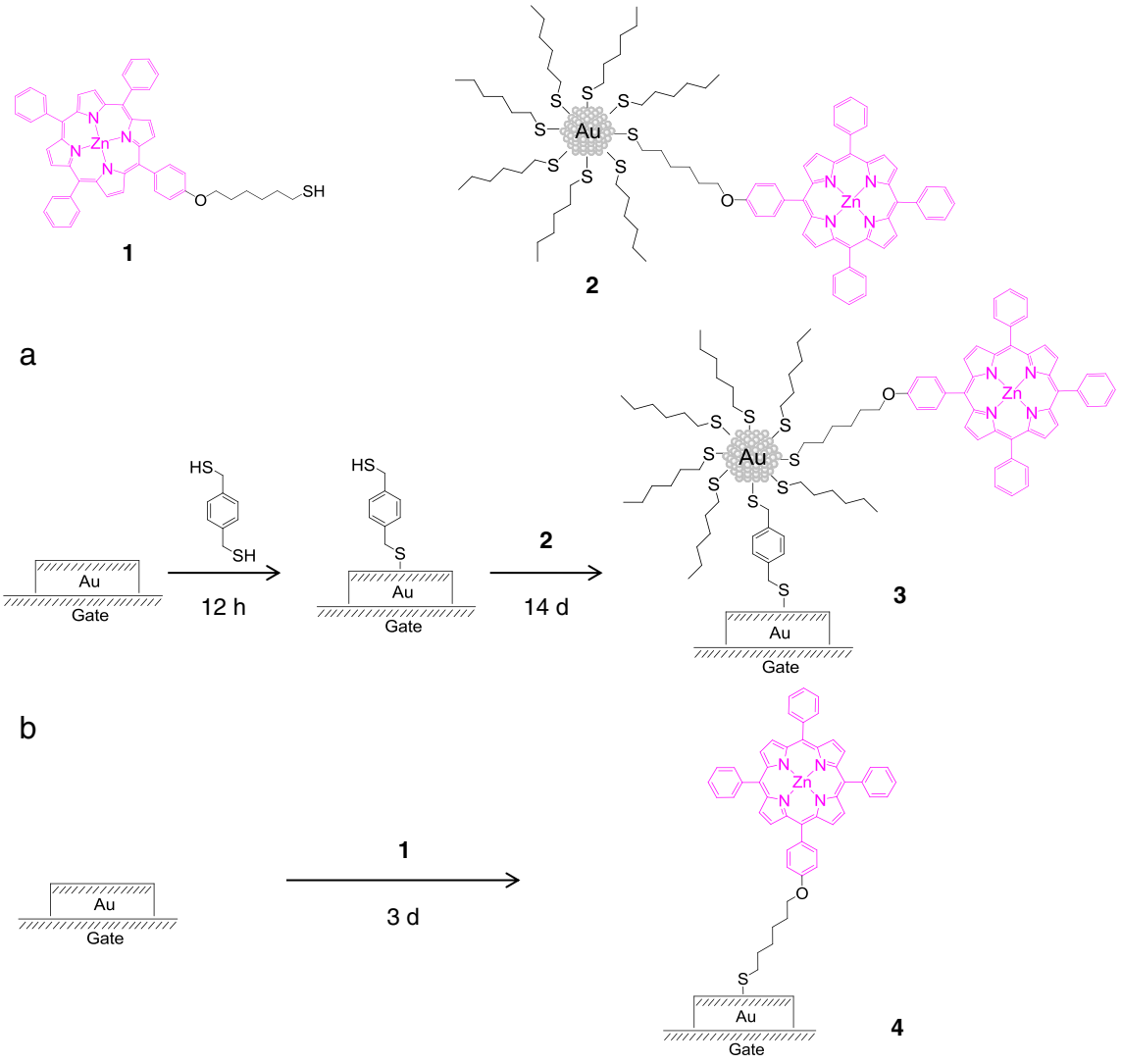

Fig. 2. Immobilization of species on the Au gate electrode modified with (a) porphyrin-attached AuNPs (**3**), and (b) only porphyrin (control electrode **4**).

magnitude of the change was smaller than that shown by FET **3**. This indicates that the direction of electron flow under irradiation was the same regardless of the presence of Au nanoparticles and that small voltage change represents a lack of electron storage derived from the SET of the Au nanoparticles.

Fig. 5 outlines the energy levels of this FET system [29,30]. The energy level of S_0, S_1, and S_2 was determined in reference to the UV–Vis spectra and the cyclic voltammogram data in Fig. S2 and S3 in the Supplementary data. First, porphyrin **1** receives light energy and transfers an excited electron to BnBr, a sacrificial reagent. Next, the holes in the porphyrin **1** are neutralized via electron transfer from the AuNPs. The electron energy level in the AuNPs is discrete because of quantum size effects, which lead to the potential jump of the electrode. This potential jump, which is derived from SET, leads to the 6–7 mV change of the modified gate of FET **4** under irradiation. The potential gap between each energy level in the AuNPs has been

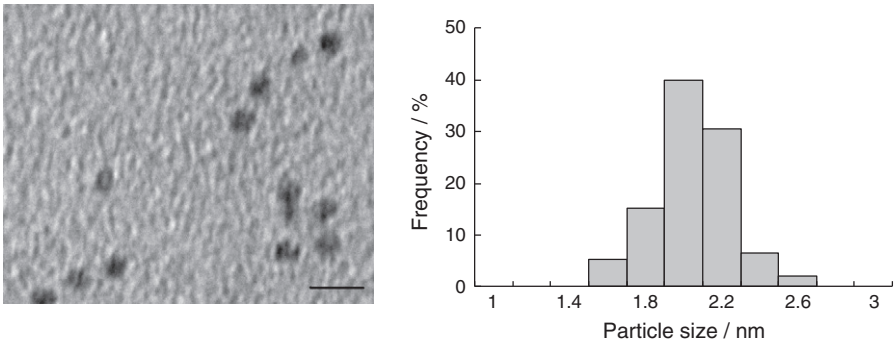

Fig. 3. TEM image and size distribution of porphyrin-attached AuNPs **2**. Scale bar is 5 nm.

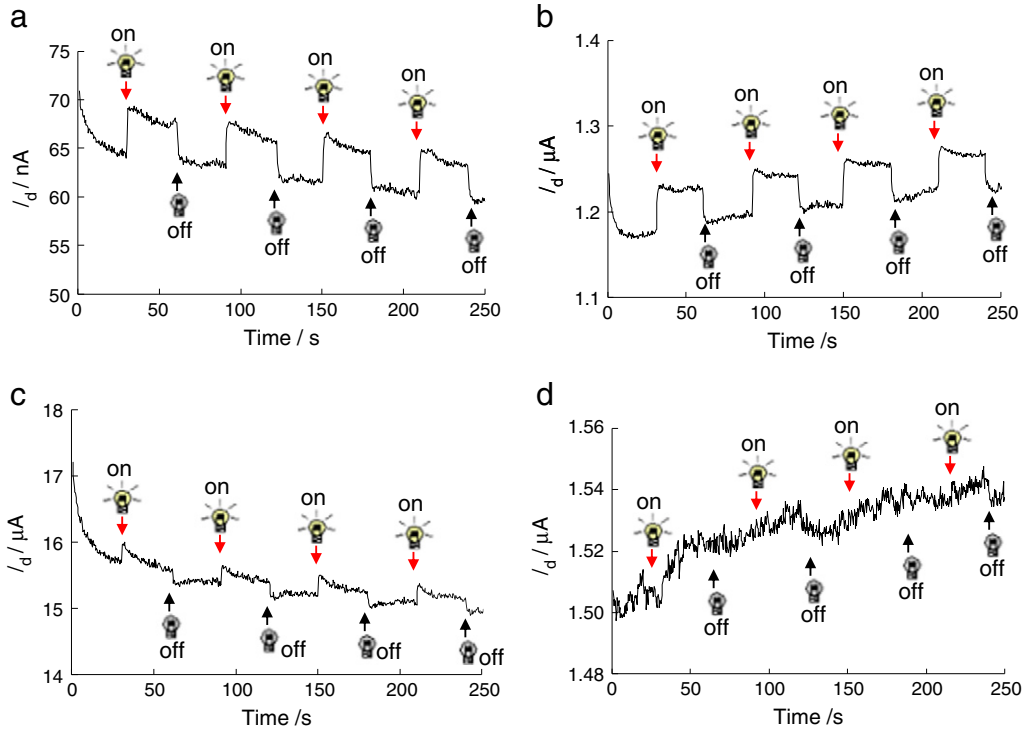

Fig. 4. I_d–t plots of modified FETs. (a) FET **3** at $V_{ref} = -0.45$ V. (b) FET **3** at $V_{ref} = -0.15$ V. (c) FET **3** at $V_{ref} = +0.45$ V. (d) Control FET **4** without AuNPs.

previously reported to be up to 0.2 V in organic electrolyte [8]. However, this system showed a smaller voltage change than shown by other previously reported AuNP systems. Comparison of the magnitude of the voltage change between the FET with nanoparticles and the control system without nanoparticles, clearly demonstrates that the enhancement of voltage change was due to the nanoparticles. Back electron transfer from porphyrin **1** to the nanoparticles likely reduced the voltage change. In the current system, an additional molecule was added to rectify the electron transfer pathway (e.g., the attachment of electron acceptor molecules to the porphyrin) and so restrain back electron transfer and increase the voltage change. This kind of molecular attachment gives this system the advantage of compatibility with organic electrolyte.

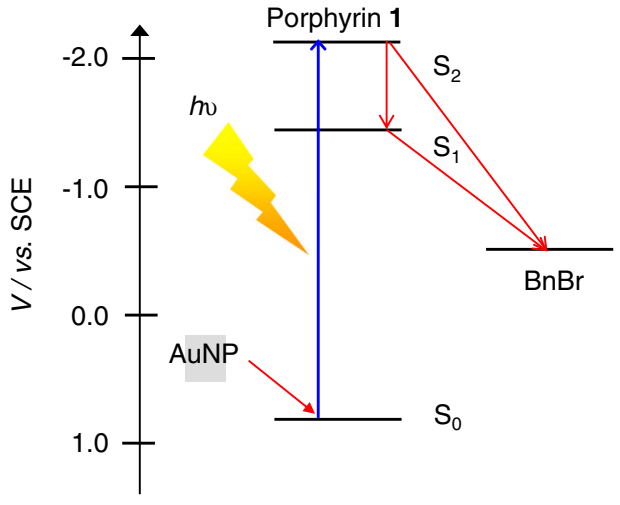

Fig. 5. Energy levels of the system.

4. Conclusions

We have demonstrated the photoresponse of an FET containing AuNPs protected with porphyrin **2**. The creation of the system was inspired by photo-electron transfer in photosynthesis. The AuNPs **2** were immobilized onto the gate of an FET, and the modified gate showed photoresponses via positive voltage changes. This voltage change is derived from SET due to the quantum size effects of the AuNPs. Further functionality may be achievable by this system and similar systems via the addition of other functional molecules, giving the system further potential advantages in addition to its compatibility with organic electrolyte.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.bbabio.2013.11.012.

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