

## Phthalocyanine-Gold Particle Nanostructured Assemblies for Near-IR Photoelectric Conversion

Sunao Yamada<sup>1\*</sup>, Kazuma Inoue<sup>2</sup>, Tsuyoshi Akiyama<sup>1</sup>, Yutaka Kuwahara<sup>2</sup>,  
Nao Terasaki<sup>2</sup>, Satoshi Nitahara<sup>2</sup> and Shinobu Inoue<sup>3</sup>.

<sup>1</sup>Department of Applied Chemistry, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

Fax: 81-92-642-3579, e-mail: sunaotcm@mbox.nc.kyushu-u.ac.jp

<sup>2</sup>Department of Materials Physics and Chemistry, Kyushu University,  
Hakozaki, Fukuoka 812-8581, Japan

<sup>3</sup>Material Science Laboratory, Mitsui Chemicals, Inc.,  
Nagaura, Sendagaya, Chiba, 299-0265, Japan.

Phthalocyanine has intensive light absorptivity in the far-red/near-IR region. In the present study, we have fabricated multistructure assemblies of a thiol derivative of phthalocyanine and gold nanoparticles on the gold electrode. Morphological and electrochemical investigations have been carried out. In the presence of oxygen, photocurrents were observed in the cathodic direction. Photocurrent action spectra were well correlated with the absorption spectrum in solution. The photocurrent increased with the active surface area of the nanoporous electrode.

Key words: gold nanoparticle, phthalocyanine, self-assembled monolayer, photocurrent

### 1. INTRODUCTION

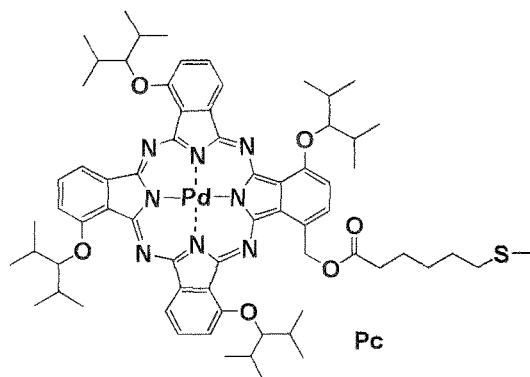
Phthalocyanines possess intensive light absorption in the far-red/near-IR (infrared) region, excellent chemical and light stability, and appropriate redox potentials against redox reactions [1]. Thus, they have been utilized as the sensitizers for dye-sensitized photoelectrochemical solar cells [2], solid-state solar cells [3], and so on, using far-red/near-IR light.

As to photoelectric conversion, the combination of sulfur-containing dyes and gold nanoparticle multistructures fabricated on a conductive support has been successful for improving photocurrent generation in the photoelectrochemical cell [4-7]. This owes to an increase in the active surface area of the electrode and to efficient immobilization of thiol derivative of photofunctional dyes by using gold-sulfur (Au-S) self-assembling. In order to further improve the efficiency of light harvesting, especially for far-red/near-IR light, applications of phthalocyanines to the above-described dye-gold particle multistructures are quite fascinating.

From these viewpoints, we have fabricated the multistructure assemblies of a thiol derivative of phthalocyanine, **Pc**, and gold nanoparticles. Appreciable photocurrents due to photoexcitation of **Pc** were obtained.

### 2. EXPERIMENTAL SECTION

Synthetic procedures of a thiol derivative of Phthalocyanine (**Pc**) have been described previously [8]. Gold nanoparticles were prepared according to the pre-



vious method [9]. Briefly, 950 ml of an aqueous chlorauric acid (HAuCl<sub>4</sub>) (0.11 g l<sup>-1</sup>) was refluxed and 50 ml of 1 % sodium citrate solution was added to the boiling solution. The mean diameter of the particles, analyzed from transmission electron micrograph images, was 16 ± 4 nm.

Figure 1 shows the schematic diagram of the experimental apparatus for preparing gold-particle nanostructures on the planar gold electrode, denoted as **GP/Au** (where *i* stands for the volume of colloidal gold solution: 20 ml for *i* = 1, 40 ml for *i* = 2, or 60 ml for *i* = 3, used for preparing **GP/Au**). The planar gold substrate (GS) was prepared by vacuum deposition of titanium followed by gold onto a glass plate (1.5 × 1.0 × 0.1 cm) at 300°C. This gold substrate was placed at the bottom of a glass vessel as shown in Fig. 1. Then, 20, 40, or 60 ml of the colloidal gold solution was added. Subsequently, 2, 4, or 6 ml of an aqueous NaClO<sub>4</sub>

solution was added at once in the colloidal solution, resulting precipitation (salting-out) of gold nanoparticles onto the surface of gold substrate. After removing the solution, the substrate was rinsed with water, and then dried in air. Accordingly, the nanostructured gold electrode, **GP<sub>i</sub>/Au**, was obtained.

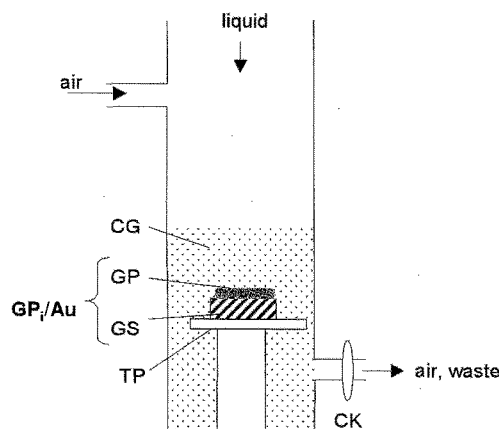


Fig. 1. Schematic diagram of experimental apparatus for preparing gold nanostructures on the gold electrode (**GP<sub>i</sub>/Au**;  $i = 1, 2, 3$ ): CG, colloidal gold solution (20 ml for  $i = 1$ , 40 ml for  $i = 2$ , 60 ml for  $i = 3$ ); GP, precipitated gold particles; GS, planar gold substrate; TP, Teflon plate; CK, cock for drain.

As a next step, the **GP<sub>i</sub>/Au** electrode was immersed into a  $\text{CH}_2\text{Cl}_2$  solution of **Pc** ( $1 \times 10^{-3}$  M) for five days to self-assemble **Pc** on the gold surface. After that, the electrode was rinsed with  $\text{CH}_2\text{Cl}_2$  and dried in air, to obtain **Pc-GP<sub>i</sub>/Au**. In a similar manner, **Pc** was self-assembled on the surface of planar gold electrode, denoted as: **Pc/Au**. In order to evaluate the active gold surface area of the nanostructured gold electrode, **GP<sub>i</sub>/Au**, cyclic voltammetric measurements of the **GP<sub>i</sub>/Au** (working) electrode were carried out using a platinum counter electrode and an ( $\text{Ag} | \text{AgCl} | \text{sat. KCl}$ ) reference electrode in aqueous 1 M  $\text{H}_2\text{SO}_4$ . Photocurrent measurements were carried out under aerobic condition. Other conditions were same as those reported previously [6,7].

### 3. RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images of the **GP<sub>i</sub>/Au** ( $i = 1, 2, 3$ ) electrodes prepared from 20, 40, and 60 ml of the colloidal gold solutions are shown in Fig. 2. All images (top view: a, c, e) show that the gold particles agglomerate and form islands (bright sites) on the planar electrode (dark sites). Macroscopically, distribution of the islands seem to be homogenous in the whole area of the electrode. The cross sectional image (b, d, f) also reflects the morphology of a part of the perpendicular layer. The thickness of the precipitates increased with increasing the volume of the colloidal

solution used. Unfortunately, absorption spectra of the **GP<sub>i</sub>/Au** electrodes are not clear because of thick precipitation and high degree of agglomeration of gold particles as described before [6, 7].

In order to evaluate the active gold surface area of **GP<sub>i</sub>/Au** electrode, cyclic voltammetric measurements of the **GP<sub>i</sub>/Au** electrode were carried out in 1 M  $\text{H}_2\text{SO}_4$ . The results are shown in Fig. 3. The active gold surface area was determined from coulombic integration of the reductive waves of gold oxide [7]. The relative surface areas as compared with the planar electrode (**Au**) were as follows: **GP<sub>3</sub>/Au**: **GP<sub>2</sub>/Au**: **GP<sub>1</sub>/Au**: **Au** = 40: 26: 12: 1.

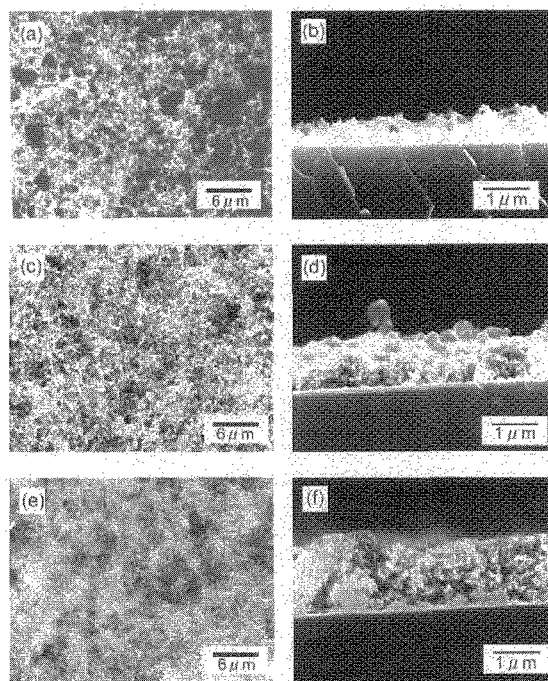


Fig 2 SEM images of **GP<sub>i</sub>/Au** electrodes prepared by precipitation of gold nanoparticles from the colloidal solutions: (a, b), **GP<sub>1</sub>/Au**; (c, d), **GP<sub>2</sub>/Au**, (e, f), **GP<sub>3</sub>/Au**. Cross sectional images are (b), (d), and (f).

In contrast with the case of a ruthenium-complex-viologen linked compound [7], the degree of immobilization of **Pc** could not be determined from cyclic voltammetry because **Pc** showed no clear redox peaks in the 0 – -0.9 V region. However, previous studies showed that the degree of immobilization of the above-described compound was roughly proportional to the volume of the colloidal solution used for the preparation of **GP<sub>i</sub>/Au** (that is, proportional to the active surface area) [6,7]. Thus, we have assumed that the degree of **Pc** immobilization is proportional to the active surface area of **GP<sub>i</sub>/Au** electrode.

Photocurrent action spectra and applied potential dependences of photocurrents at 700 nm are shown in Fig. 4. Each **Pc**-modified electrode showed clear peaks corresponding with those of absorption spectrum in

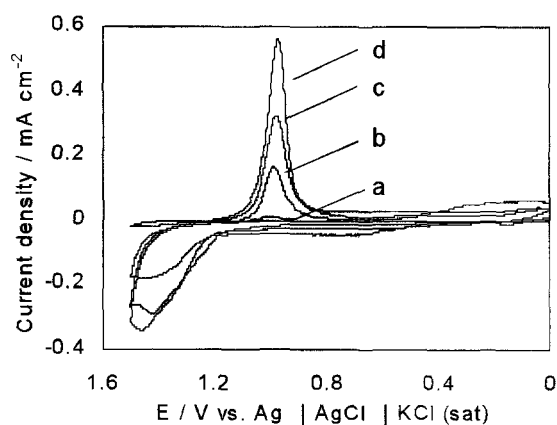


Fig. 3 Cyclic voltammograms of the Au and GP<sub>i</sub>/Au electrodes in aqueous 1 M H<sub>2</sub>SO<sub>4</sub> (scan rate, 0.01 Vs<sup>-1</sup>): a, Au; b, GP<sub>1</sub>/Au; c, GP<sub>2</sub>/Au; d, GP<sub>3</sub>/Au.

solution. Thus, the photocurrent is induced by photoexcitation of Pc. As shown in Fig. 4b, the photocurrent was observed in the cathodic direction in the potential region of -0.1 to 0.3 V. It also decreased with increasing the applied potential. These photocurrent results lead to the photocurrent generation mechanism as shown in Fig. 5. The photoexcited state of Pc gives an electron to oxygen in the bulk, and the generated Pc cation accepts the electron from the electrode. The IPCE

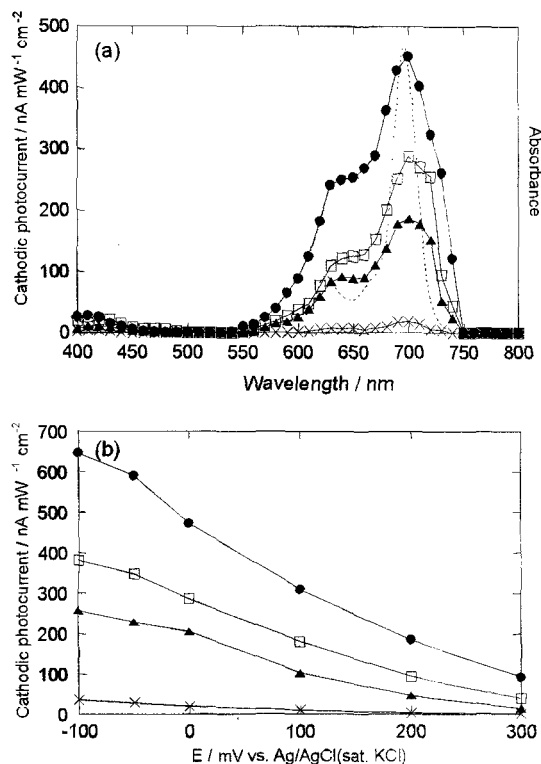


Fig. 4 Cathodic photocurrent action spectra (a) and applied potential dependences at 700 nm (b) of Pc/Au and Pc-GP<sub>i</sub>/Au electrodes: ×, Pc/Au; ▲, Pc-GP<sub>1</sub>/Au; □, Pc-GP<sub>2</sub>/Au; ●, Pc-GP<sub>3</sub>/Au

(incident photon-to-current conversion efficiency) value for the GP<sub>3</sub>/Au electrode was ~0.1 %, as determined from the photocurrent (450 nA·cm<sup>-2</sup> at 700 nm, Δλ = ± 16 nm, E = 0V).

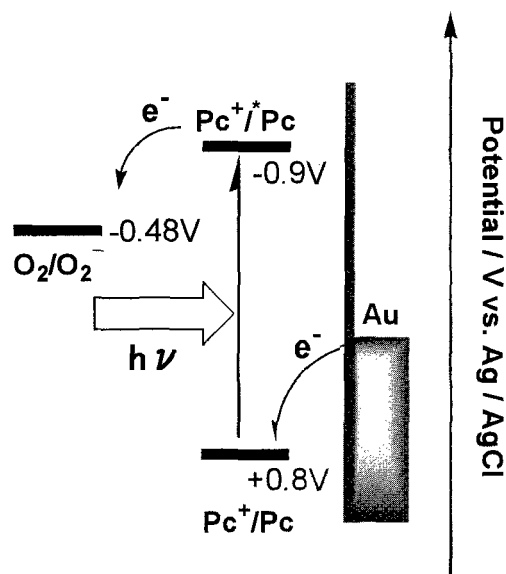


Fig. 5. Photocurrent generation diagram

Figure 6 shows the relative photocurrent at 700 nm from the Pc-GP<sub>i</sub>/Au electrode and the active surface area of the GP<sub>i</sub>/Au as a function of the volume of colloidal solution used for preparing the GP<sub>i</sub>/Au electrode. In order to clarify the relationship, the photocurrent and the total surface area of the planar electrode were normalized to unity. Both photocurrents and total surface areas increased with increasing the volume of colloidal solution, indicating the formation of similar gold particle nanostructures in all GP<sub>i</sub>/Au electrodes. However, the photocurrent was not so large as that expected from the total surface area. This may, at

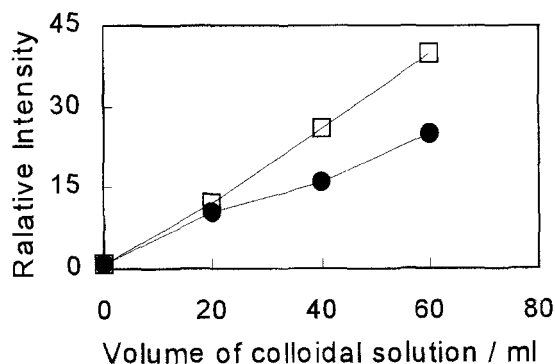


Fig. 6. Relative increase in the surface area (□) and photocurrent at 700 nm (●) as a function of the volume of colloidal gold solution used for preparing GP<sub>i</sub>/Au electrode.

least in part, due to insufficient penetration of the irradiation light in the gold-particle nanostructure with increasing the layer thickness. Thus, the change in the size of gold nanoparticle will be a key for improving photocurrent generation.

In conclusion, we have prepared the self-assembled nanolayer of near-IR sensitive phthalocyanine dye on the surface of gold-particle nanostructure. Clear photocurrent responses due to photoexcitation of **Pc** were observed and increased with increasing the active surface area of the nanostructured electrode. Thus, the combined immobilization of visible-sensitive dyes and far-red/near-IR sensitive phthalocyanine will improve the total photocurrent generation efficiency in wider wavelength regions. The work is in progress along this line.

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#### 4. REFERENCES

- [1] "Phthalocyanines: Properties and Applications", Vol.4, Eds. By C. C. Lezanoff and A. B. P. Lever, VCH, Weinheim (1996).
- [2] J. He, G. Benko, F. Korodi, T. Polivka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeld and V. Sundström, *J. Am. Chem. Soc.*, **124**, 4922-32 (2002).
- [3] M. Hiramoto, H. Fujisawa and M. Yokoyama, *J. Appl. Phys.*, **72**, 3781-87 (1992).
- [4] Y. Kuwahara, T. Akiyama and S. Yamada, *Thin Solid Films*, **393**, 273-77 (2001).
- [5] S. Yamada, T. Tasaki, T. Akiyama, T. Terasaki and S. Nitahara, *Thin Solid Films*, **438/439**, 70-4 (2003).
- [6] Y. Kuwahara, T. Akiyama and S. Yamada, *Langmuir*, **17**, 5714-16 (2001).
- [7] T. Akiyama, K. Inoue, Y. Kuwahara, N. Terasaki, Y. Niidome and S. Yamada, *J. Electroanal. Chem.*, **550/551**, 303-07 (2003).
- [8] Japanese patent (No2003-123863).
- [9] K. C. Grabar, R. G. Freeman, M.B. Hommer and M. J. Natan, *Anal. Chem.*, **67**, 735-43 (1995).

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