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Fabrication of Porphyrin-Gold Nanoparticle Multistructures for Photoelectric Conversion

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1. Introduction

Fabrication of three-dimensional hybrid materials consisting of organic dyes and nanometer-sized metal particles has been extremely important in the development of nanoscale optoelectronic devices [1]. For those applications, the use of gold nanoparticle multistructures is a very promising prospect, because they are basically passive structural elements and can offer nanoporous (high surface area) electrodes. Quite recently, we developed novel methods of fabricating ruthenium complex - gold nanoparticle multistructures by using the self-assembling technique [2, 3]. As to organic dyes, absorptivity of light as well as redox power will be needed to achieve higher efficiencies of photoelectric conversion. A noteworthy advantage of porphyrin is that it has very high absorptivity. From these viewpoints, we have fabricated multistructured assemblies consisting of a porphyrin dye and gold nanoparticles and have found clear photocurrent responses from them.

2. Experimental

A tetrathioacetylporphyrin (TP) was prepared in our laboratory. Gold nanoparticles (AuP) were prepared according to the previous method [4]. Briefly, an aqueous solution of chlorauric acid (HAuCl₄) (25 mg/19 ml) was refluxed and 10 ml of 1% sodium citrate solution was added to the boiling solution. The mean diameter of the particles, analyzed from transmission electron micrograph, was 16±4 nm. Absorption and photocurrent measurements were carried out as described previously [3].

The preparation procedure of the multistructured assemblies on the ITO electrode is shown in Fig. 1. First, the ITO electrode was immersed into a mixed solution of 3-mercaptopropyltrimethoxysilane (MS) and toluene (3:97 v/v) to implant thiol groups at the surface (step 1). Next, the MS-modified electrode was immersed into the colloidal solution of AuP for 1 day (step 2), giving the assembly of AuP. Then, the AuP-MS-modified electrode was immersed into a chloroform solution of TP (1.5 mM) for another 1 day (step 3). By repeating these assembling cycles (steps 2 and 3), we obtained the multistructured assemblies of TP and AuP as: (TP-AuP)_n (n=1, 6) on the ITO electrode.

3. Results and Discussion

As shown in Fig. 2, absorption spectra of the assemblies have two characteristic bands around 430 nm due to the

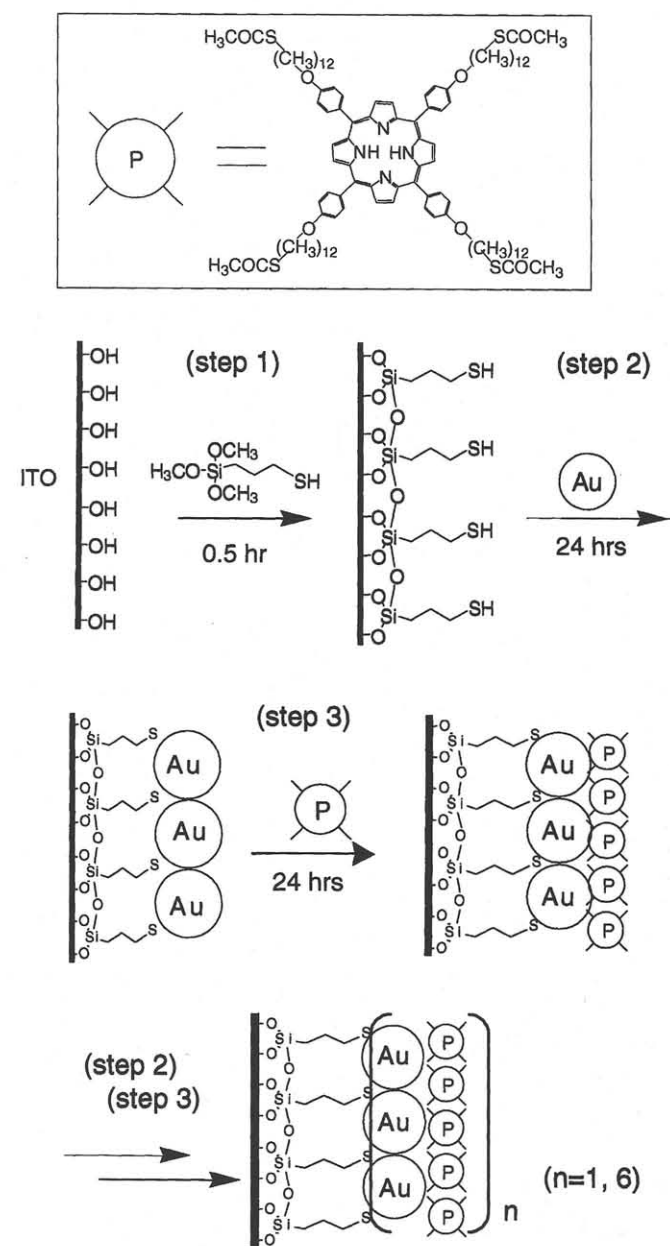


Fig. 1 Preparation procedure of the assembly

Soret band of TP and 500-570 nm region due to surface plasmon oscillation of AuP. Clearly, the both bands were

much larger for $n = 6$. The plasmon band of **AuP** for $n=6$ showed red-shift and somewhat broadening as compared with that for $n=1$, due to interparticle plasmon coupling [5].

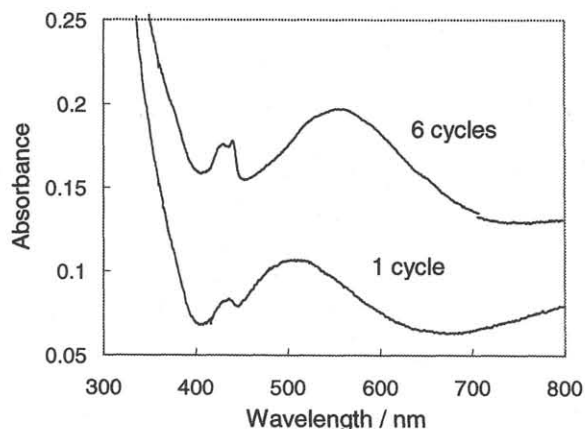


Fig.2 Absorption spectra of **(TP-AuP)_n** assemblies: $n = 1, 6$.

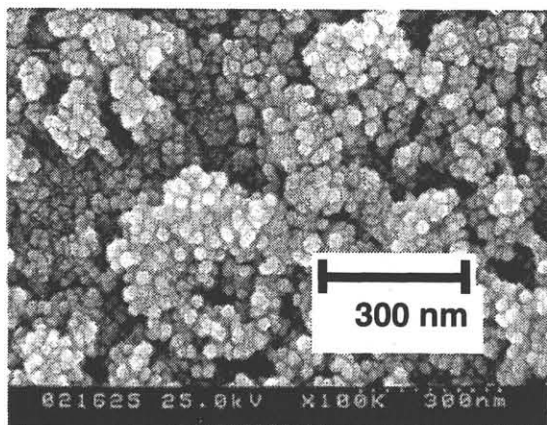


Fig. 3 SEM photograph of **(TP-AuP)₆** assembly

The morphology of the assembly was investigated by scanning electron micrograph (SEM). The results for the **(TP-AuP)₆** assembly is shown in Fig. 3. With increasing the assembling cycles, **AuP** tended to agglomerate heterogeneously. The XPS measurements also revealed the presence of Au-S bonding.

Photocurrent action spectra of the assemblies were measured under air-saturated condition. As shown in Fig. 3, the photocurrent was observed in the cathodic direction at 0 vs. Ag/AgCl. As for $n=6$, the action spectrum showed a peak around 430 nm corresponding to the Soret band of **TP** (Fig. 2). It also showed a very broad band in the 450-600 nm region, probably due to the effect of surface plasmon oscillation. The predominant mechanism for photocurrent generation is shown in Scheme 1. The key step is the photoinduced electron-transfer from the photoexcited **TP** to oxygen, because the photocurrent is observed in the cathodic direction. Smaller photocurrents at longer wavelengths must be generated by another pathway(s). Detailed studies on the photocurrent mechanism are underway.

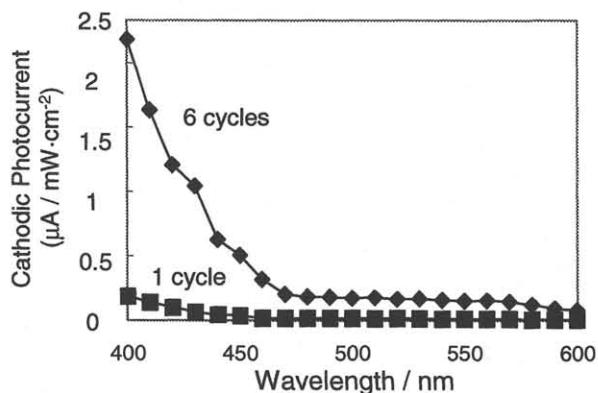
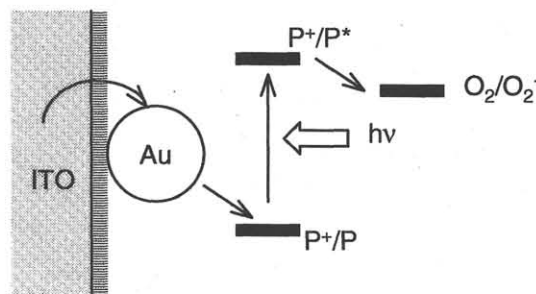


Fig. 4 Photocurrent action spectra of **(TP-AuP)_n** assemblies: $n=1, 6$. $E=0V$ vs Ag/AgCl.



Scheme 1

References

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