Effects of Nanoporous Morphology on the Photoelectrochemical Responses from Dye-Gold Nanoparticle Multistructures

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Multistructure assemblies consisting of a photoresponsive dye and gold nanoparticles were prepared by precipitation and subsequent self-assembling processes. Morphological and (photo)electrochemical properties of the dye-modified multistructures were compared in some different precipitation conditions. Scanning electron microscopy measurements revealed that the highly nanoporous structures were obtained when the precipitation was carried out at 100°C, which gave substantially larger photocurrent responses.

Key words: gold nanoparticle, self-assembled monolayer, photocurrent, morphology, conductivity

1. INTRODUCTION

Fabrication of three-dimensional materials consisting of organic dyes and nano meter-sized metals and (or) semiconductors has been extremely important in the development of nanoscale optoelectronic devices. For those applications, the use of nanoparticle multistructures is a promising prospect, because they can offer nanoporous (high surface area) electrodes [1,2]. Especially, gold nanoparticles are very attractive because they are passive structural elements and have unique optical properties based on localized surface plasmon oscillation in the visible-infrared region Thus, applications of this surface plasmon [3]. oscillation for optoelectronic devices are quite interesting. The key process is the excitation of organic molecules bound at the gold surface with the surface plasmon electromagnetic wave [4-6]. To make the most of this excitation process, one has to build up tailormade multistructures with appropriate spatial alignments.

Recently, we first reported multistructures consisting of thiol dyes and gold nanoparticles on the planar electrode and their photocurrent responses [6-9]. We have developed two methods for constructing dye-gold particle multistructures on the electrode: (1) alternate self-assembling of the dye and the gold nanoparticles [6,7], and (2) a precipitationself-assembling process [8,9]. The latter method is simpler and substantial increase in the number of immobilized dyes per projective surface area has been achieved as compared with the former one.



In the present study, we have investigated the effects of some preparation conditions on the structural properties of multistructures and their photoelectrochemical responses.

2. EXPERIMENTAL

The preparation procedure of **RuVS** has been described previously [10]. Chloraulic acid (HAuCl₄·4H₂O) and other chemicals were used as received. An aqueous solution of gold nanoparticles was prepared by the reduction of HAuCl₄ with sodium citrate as before [11]. The planar gold electrode was obtained from Geomatec; it was prepared by vacuum deposition of gold onto transparent mica plate (Furuuchi chemical Co.).

The preparation procedure of a modified electrode with **RuVS** and gold nanoparticle nanostructures is based on the combination of salting-out and self-assembling procedures. The preparation procedure of gold nanoparticle multistructures on the planar gold electrode is schematically shown in Fig. 1, and the preparation conditions are summarized in Table 1.

Sample	Volume (ml) ^{a)}	Concentration $\times 10^{-5}$ (M) ^{b)}	Temperature (°C) ^{c)}	Resistance $\times 10^{-2} (\Omega)^{d}$	Surface Coverage ^{e)} $\times 10^{-9}$ (mol/cm ²)	Photocurrent intensity ^{f)} (µA/cm ² mW)
A (<u>A</u>)	0	0		6.5	(0.30)	(8.5)
B (<u>B</u>)	20	26.7	r.t.	6.6	(1.6)	(28)
C (<u>C</u>)	60	26.7	r.t.	5.1	(3.1)	(67)
D (<u>D</u>)	20	26.7	~100	6.9	(1.8)	(68)
E (<u>E</u>)	60	8.91	r.t.	5.4	(1.9)	(44)

 Table 1
 Preparation conditions and properties of modified gold electrodes

a) Volume of gold colloidal solution, used for precipitation.

b) Concentration of gold colloidal solution, used for precipitation, is shown as the gold atom.

c) Temperature in the precipitation process.

d) Resistance of gold substrate and gold nanosuructured layers, measured by the four-probe method.

e) Evaluated from the integration of the CV curves of V^{2+}/V^+ redox couple.

f) Measured at 0V vs. Ag/AgCl with 460 nm light irradiation.



Fig. 1. Schematic illustration for preparing gold-nanoparticle multistructures on the planar electrode. AuP: gold nanoparticle.

First, the planar gold electrode (denoted as A) was placed at the bottom of a flat-bottomed glass vessel (3.6 cm inner diameter), and 20 or 60 ml of the colloidal gold solution was added. Then, 2 or 6 ml of a saturated aqueous NaClO₄ solution was added at once to induce precipitation (salting-out) of gold nanoparticles on the surface We have compared three experimental of A. conditions: (1) volumes of colloidal solutions between 20 and 60 ml under the identical concentrations of gold nanoparticles (B vs C), (2) salting-out temperatures between a room temperature and 100°C (B vs D), and (3) concentrations of colloidal solutions between 26.7 and 8.91×10^{-5} M (B vs E) at a room temperature. After leaving overnight, the solution was removed and the electrode was rinsed with water, followed by drying under nitrogen gas. As a next step, the planer (A) and nanostructure electrodes (B, C, **D** and **E**) were immersed into a CH_3CN solution of **RuVS** $(1 \times 10^{-3} \text{ M})$ for three days to self-assemble RuVS on the gold surfaces, giving RuVSmodified electrodes as: A, B, C, D and E.

Electrochemical and photoelectro- chemical responses of the nanostructures and the corresponding **RuVS**-modified electrodes were investigated with a three-electrode

(photo)electrochemical cell prepared in our Cyclic voltammetric (CV) laboratory [6-9]. modified measurements of the (working) electrodes were carried out using a platinum counter electrode and a Ag/AgCl (sat. KCl) reference electrode in a 0.1 M NaClO₄ aqueous Photocurrent measurements were also solution. carried out with the same cell in an aqueous solution containing sodium L-ascorbate (AsNa) as a sacrificial reagent (0.05 M). The light from a Xenon lamp (LAX100, Asahi Spectra Co.), passed through an optical filter (Asahi Spectra Co.), irradiated the modified (working) electrode and the resultant photocurrent was measured by a potentiostat (ALS, model-610A).

Scanning electron micrographs (SEMs) were obtained with Hitachi S-5000 microscope. Absorption spectra were recorded on a Shimadzu UV-2500 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 SEM measurements

Figure 2 shows SEM images of the RuVS-modified electrodes. As can be recognized from the images, most of the gold particles are agglomerated with each other in all The degree of agglomeration was almost cases. unchanged when only the volume of the colloidal solution was different (B vs C). However, the degree of agglomeration and fusion was different when the precipitation temperature and the concentration of colloidal solution were different. When the precipitation was carried out at 100°C, almost gold nanoparticles were substantially fused with peanut-like morphology and formed highly nanoporous multistructures (D). On the other hand, the size and the shape of initial nanoparticles were almost kept unchanged when the precipitation was carried out with the diluted gold colloidal solution (E). Mean resistances of the gold nanoparticle multictructures, measured by the four-probe method, were nearly same in all samples within $(5-7) \times 10^{-2}$ Ω. Thus, all multistructures have enough conductivity as the electrode materials.

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Fig. 2. SEM images of the **RuVS**-modified nanostructured electrodes: **<u>B</u>**, <u>**C**</u>, <u>**D**</u> and <u>**E**</u>.

Thus, we have investigated the electrochemical and photoelectrocheical responses from the **RuVS**-modified electrodes: <u>A</u>, <u>B</u>, <u>C</u>, <u>D</u> and <u>E</u>.

3.2 Electrochemical measurements

Figure 3 shows CV waves of the **RuVS**-modified electrodes in the 0 - -0.8 V region. The redox couple at $E_{1/2} = -0.47$ V is characteristic of the first reduction of the viologen moiety (V^{2^+}/V^+) of **RuVS**. The coverage of **RuVS** was evaluated from the coulometric analysis of the reduction wave. The results are summarized in Table 1. The coverage of RuVS was larger when the volume of colloidal solution used for precipitation was larger. However, the peak separation became larger with increasing the degree of multistructuring (Fig. 3 (a)). On the other hand, the coverages were nearly identical between \underline{D} and \underline{E} , and were slightly larger than \underline{B} . This is quite reasonable because the total amount of gold nanoparticles for precipitation is identical in the three electrodes (see Figure 3 (b) and Table 1). In addition, the agglomerates seem to be somewhat congested in \mathbf{B} , as compared with \mathbf{D} and E, from the SEM images.

3.3 Photoelectrochemical measurements

In the presence of 0.05 M AsNa, anodic photocurrents were clearly observed at E=0 V vs. Ag/AgCl. Figure 4 (a) shows photocurrent action spectra from the **RuVS**-modified electrodes. The spectral shape is well overlapped with the corresponding absorption spectrum of **RuVS** in acetnitrile (Abs. of RuVS in (a)). This clearly shows that the photocurrent is induced by photoexcitation of the tris(2,2'-bipyridine) ruthenium (Ru²⁺) moiety. That is, photoinduced electron-transfer from the photoexcited Ru²⁺ (*Ru²⁺) to V²⁺ generates Ru³⁺ and V⁺. The generated Ru³⁺ is reduced by AsNa, while the



Fig. 3. CV waves of **RuVS**-modified nanostructured electrodes (\underline{B} , \underline{C} , \underline{D} and \underline{E}) and the **RuVS**-modified planar electrode (\underline{A}). Scan rate: 0.1 V/s.

reduced species V^+ gives the electron to the electrode, generating anodic photocurrents. The photocurrent mechanism and the electron flow are illustrated in Fig. 4 (b).

It is clear that the photocurrent increased with increasing the volume of colloidal solution used for precipitation (\underline{B} vs \underline{C}), and were The result is considerably larger than that of <u>A</u>. quite consistent with the immobilized number of RuVS (Table 1). However, considerable difference in the photocurrent intensity was observed in \underline{B} , \underline{D} and \underline{E} , in spite that the total amount of gold nanoparticles used for precipitation was identical. Especially, D showed a larger photocurrent than that expected from the number of immobilized RuVS (Table 1). This may attributed to the formation of highly nanoporous multistructures in **D**, which is favorable for the diffusion of the sacrificial reagent as well as the electrolyte. Furthermore, the incident light may be able to penetrate into the inside of multistructure more smoothly, as compared with the others. Thus, control of the morphology of multistructure is very important to obtain larger photocurrent responses in the dye-gold nanoparticle assemblies.



Fig. 4. (a) Photocurrent action spectra from **RuVS**-modified nanoatructured electrodes (**<u>B</u>**, <u>**C**</u>, <u>**D**</u> and <u>**E**</u>) and the **RuVS**-modified planar electrode (<u>**A**</u>). Conditions: E=0 V vs. Ag/AgCl, $\Delta\lambda = \pm 6.5$ nm, [AsNa] = 0.05 M, [NaClO₄] = 0.1 M. (b) Energy diagram for photocurrent generation.

4. CONCLUSION

The present study demonstrated that the morphology of gold nanoparticle multistructures could be controlled by the experimental condition for the precipitation of gold nanoparticles on the planar electrode. The highly nanoporous structures were obtained when the precipitation was carried out at high temperature, and gave substantially larger photocurrent responses. The results offer an important information for fabricating highly-efficient optoelectronic devices using nanoparticles.

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