

# Photocurrent Enhancement in Porphyrin-Silver Nanoparticle Composite Films using Nanostructures of Silver Nanoparticles

R. Matsumoto<sup>1</sup>, S. Yamada<sup>2</sup>, H. Yonemura<sup>2</sup>

<sup>1</sup>Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka 819-0395, Japan.

Phone: +81-92-802-2816 E-mail: Ryuji@mail.cstm.kyushu-u.ac.jp

<sup>2</sup>Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan

## 1. Introduction

Organic solar cells are regarded as promising technology for renewable energy production. A variety of efforts have been made to improve the efficiency of photoelectric conversion. However, the devices performance doesn't reach commercial level. In order to improve it, we focus attention on noble metal nanoparticles which are expected to excite organic dye efficiently by localized surface plasmon resonance(LSPR). In this study, we examined the effects of enhanced electric fields resulting from LSPR on the photocurrents of the tetraphenylporphyrin (TPP)-silver nanoparticle (AgP) composite films.

## 2. Results and Discussion

### 2-1. Preparation of TPP-l-AgP composite films

Large and small silver nanoparticles (l-AgP and s-AgP) were synthesized as previously described [1,2]. The average diameters of (l-AgP;50 nm and s-AgP;15 nm) were estimated from TEM images. Fig. 1 shows an extinction spectrum of the aqueous solution of l-AgP (the insert is TEM image, scale bar=50 nm). The extinction spectrum has a broad peak due to including some particle size.

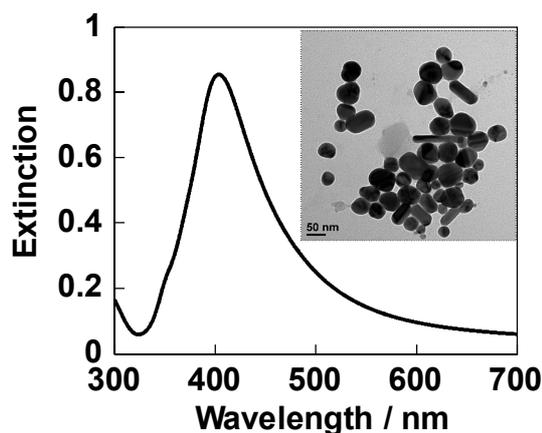


Fig. 1 Extinction spectrum of the aqueous solutions of l-AgP; (insert) TEM image of l-AgP, scale bar=50 nm).

The TPP-AgP composite films were prepared by the similar method as reported in previous paper [3]. An indium-tin-oxide (ITO) substrate was employed ultrasonic washing with acetone and 2-propanol and then cleaned in

an ozone atmosphere 30 min. The cleaned ITO was immersed in a freshly prepared solution of 3 mM polyethyleneimine (PEI) solution containing 1 M NaCl for 20 min, followed by rinsing with ultrapure water and drying (ITO/PEI). Next, ITO/PEI was immersed into the aqueous solutions of l- or s-AgP for different time ( $x = 0, 1, 4, 6, 12$  h) to immobilize with AgP on the ITO substrates by the electrostatic interaction (ITO/PEI/l- or s-AgP(xh)). Next, the surface of l- or s-AgP (xh) was modified by immersing into an ethanol solution of octanethiol (OT) (10 mM) (ITO/PEI/l- or s-AgP(xh)-OT) to stabilize the absorbed AgP surface. Finally, 5  $\mu$ l of a toluene solution of TPP (0.2 mM) as an organic dye was spin-coated on the ITO/PEI/l- or s-AgP(xh)-OT (ITO/PEI/l- or s-AgP(xh)-OT/TPP).

### 2-2. Fluorescence measurement of ITO/PEI/l-AgP(xh)-OT/TPP

The fluorescence spectra of ITO/PEI/l-AgP (xh)-OT/TPP were measured in order to evaluate the effect of enhanced electric field induced by LSPR of l- or s-AgP. The fluorescence intensity due to TPP enhanced in the presence of l-AgP as compared with that in the absence of l-AgP (Fig. 2). The enhancement of the fluorescence emission intensity is most likely ascribed to the enhanced electric field and strong scattering induced by LSPR. The fluorescence signal increased up to 4h of immersion time (x) and then decreased above 4h.

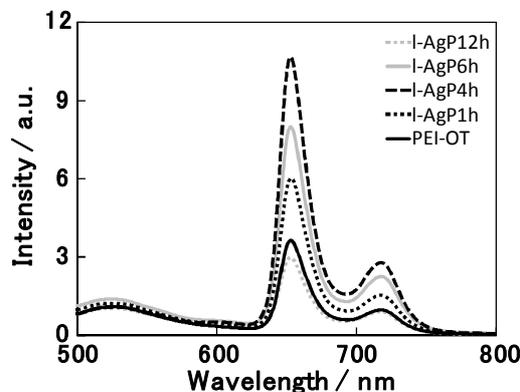


Fig. 2 Fluorescence emission spectra of ITO/PEI/l-AgP(xh)-OT/TPP( $x = 0$  (—), 1 (---), 4 (---), 6 (—), 12 (---); ( $\lambda_{em} = 420$  nm).

Fig. 3 shows the fluorescence excitation spectra of ITO/PEI/l-AgP (xh)-OT/TPP ( $\lambda_{em}=720$  nm). The spectra of ITO/PEI/l-AgP (1-12h)-OT/TPP in the presence of l-AgP are quite different from that of ITO/PEI/l-AgP (0h)-OT/TPP in the absence of l-AgP. The signals due to Q bands of TPP in the longer wavelength region ( $>500$  nm) in the presence of l-AgP increased as compared with those in the absence of l-AgP. The results strongly suggest that TPP is much more effectively excited in the plasmonic field of the aggregates of l-AgP in the longer wavelength region ( $>500$  nm).

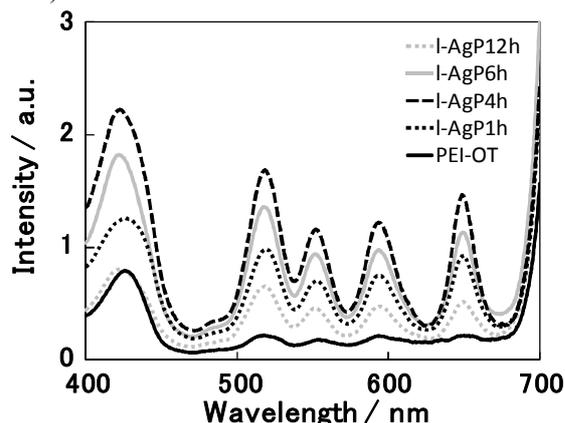


Fig. 3 Fluorescence excitation spectra of ITO/PEI/l-AgP(xh)-OT/TPP(x= 0 (—), 1(— · —), 4(---), 6(— — —), 12(·····); ( $\lambda_{em}=720$  nm).

### 2-3. Photoelectrochemical measurements of ITO/PEI/AgP(xh)-OT/TPP

The photocurrent spectra of ITO/PEI/l- or s-AgP (xh)-OT/TPP were measured in order to examine the effects of the amount and the size effect of AgP on the photocurrent in the TPP-silver nanoparticle composite films. Photocurrent measurements were carried out in an aqueous solution containing 0.1M NaClO<sub>4</sub> using the three electrode photoelectrochemical cell; the three electrodes were modified electrode as working, Ag/AgCl (sat. KCl) electrode as reference, and platinum electrode as counter. Before measurements, oxygen bubbling was carried out for 30 min.

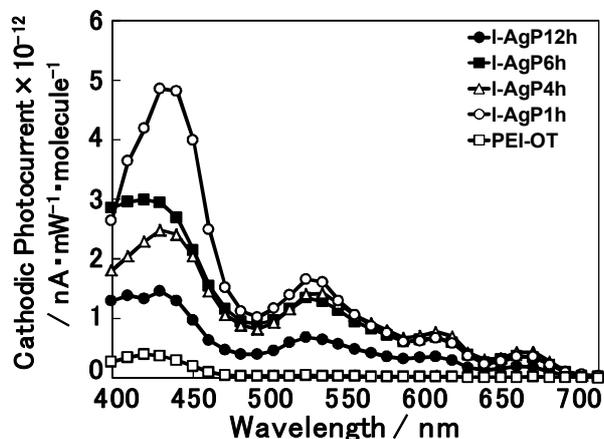


Fig. 4 Photocurrent action spectra of ITO/PEI/l-AgP(xh)-OT/TPP(x=0 (□), 1(○), 4(△), 6(■), 12(●)).

All photocurrents were measured at 0 volt vs. Ag/AgCl. All photocurrents action spectra indicated that the photocurrents are attributable to TPP (Fig. 4).

The maximum enhancement of photocurrents at immersion time of 1h was observed in ITO/PEI/l-AgP(xh)-OT/TPP. Effect of the immersion time on photocurrent is different from that on the fluorescence intensity (Fig. 2 and Fig. 3).

The photocurrent ratio of ITO/PEI/l-AgP(1h)-OT/TPP to ITO/PEI/s-AgP(2h)-OT/TPP was evaluated to verify the size effects of a localized plasmon field (Fig. 5). 4- to 9-fold enhancements of photocurrents in the ITO/PEI/l-AgP(1h)-OT/TPP were observed as compared with that in the ITO/PEI/s-AgP(2h)-OT/TPP. If the photocurrent from the ITO/PEI/l-AgP(1h)-OT/ZnTPP is generated only by simple photoexcitation of immobilized TPP molecules, the photocurrent ratio should be immobilized at all wavelength [4,5]. The result is mainly attributable to the surface plasmon of the aggregates of l-AgP.

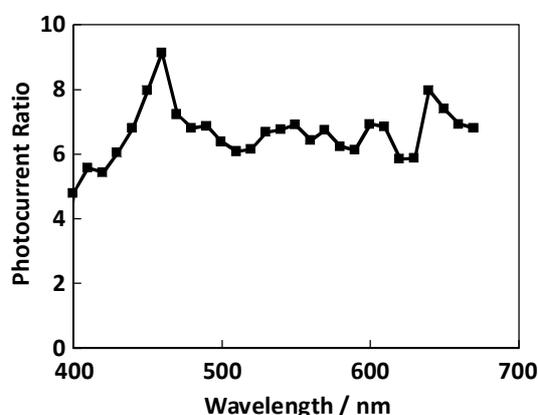


Fig. 5 Photocurrent ratio : [ITO/PEI/l-AgP(1h)-OT/TPP] / [ITO/PEI/s-AgP(2h)-OT/TPP].

### 3. Conclusions

In this study, we examined the effects of the amounts and the size of AgP in the TPP-silver nanoparticle composite films for fluorescence and photocurrent. The maximum photocurrent of ITO/PEI/l-AgP(1h)-OT/TPP was observed. The results in this study suggest the optimum condition of the amounts and the size of AgP for the photocurrents or the fluorescence of TPP-AgP composite films.

### References

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