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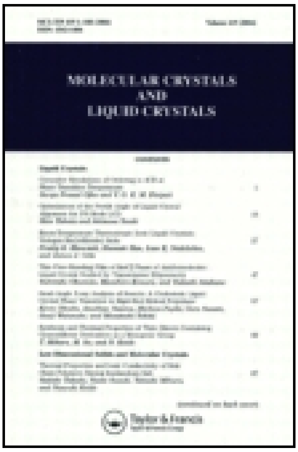

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Effects of Silver Nanoparticles on Photocurrents of Zinc Porphyrin-Viologen Linked Compound-Silver Nanoparticle Composite Films

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The fabrication of a zinc-porphyrin(ZnP)–viologen(V) linked compound with six methylene group (ZnP(6)V)–silver nanoparticle (AgP) composite films on indium-tin-oxide (ITO) electrodes were carried out by the electrostatic layer-by-layer adsorption technique. The photocurrents in ZnP(6)V–AgP composite films were larger than those in ZnP(6)V films, and were much larger than those in ZnP films as a reference. The large enhancement of the photocurrents in ZnP(6)V–AgP composite films are most likely ascribed to the combination of localized surface plasmon resonance due to AgP and photoinduced intramolecular electron-transfer due to the linking of V moiety.

Keywords Intramolecular electron-transfer; localized surface plasmon resonance; photocurrent; silver nanoparticle; viologen; zinc-porphyrin

Introduction

Photocurrent generation devices using organic compounds are expected to become the next generation solar systems. However, most important issue is to improve the efficiency of photoelectric conversion. One of the methods for upgrading these devices is the use of localized surface plasmon resonance (LSPR) induced by the coupling of the incident electric field with the free electrons in the metal [1–6].

Previously, we reported the technique of electrostatic layer-by-layer adsorption for fabricating multistructures of silver nanoparticles (AgPs). The technique is very convenient and needs no sophisticated equipment such as vacuum systems. Nevertheless, it is easy to control the deposition density of charged metal nanoparticles by the changing the immersion time of the substrate into the corresponding colloidal solution [3, 5]. Recently, we found the remarkable enhancement of photocurrent responses based on the photoexcitation of a tetraphenyl porphyrin or a palladium phthalocyanin derivative as an organic dye adsorbed onto the surfaces of AgPs; the AgP–porphyrin assemblies were prepared by the layer-by-layer technique in the organic dye–AgP composite films [3]. However, effects of AgPs

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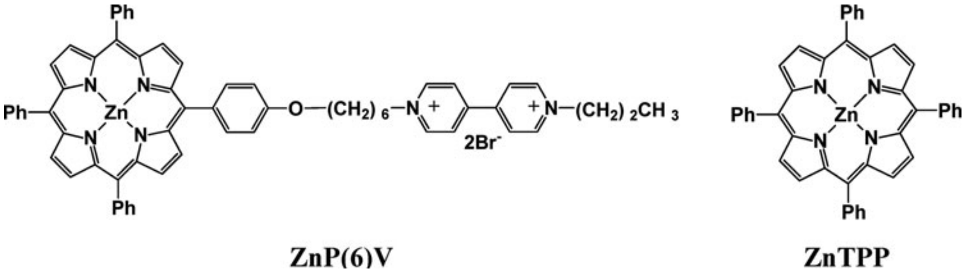

Figure 1. Molecular structures of a zinc-porphyrin–viologen linked compound with six methylene group (ZnP(6)V) and zinc tetraphenyl porphyrin (ZnTPP) as a reference compound.

on photocurrent of organic dye-silver nanoparticle (AgP) composite films using a donor-acceptor linked compound as an organic dye has not been elucidated yet.

In this study, we examined the effects of enhanced electric fields resulting from LSPR on the photocurrents of donor-acceptor linked compound–AgP composite films using a zinc porphyrin(ZnP)–viologen(V) linked compound (ZnP(6)V) with six methylene group to elucidate the mechanism of the effect of LSPR due to AgPs.

Experimental

Silver nitrate ($AgNO_3$, Wako), trisodium citrate dihydrate (Wako), poly(ethyleneimine) (PEI, Mw = 50,000–100,000, Wako), octanethiol (OT, TCI), and other chemicals were used as received. Amphiphilic ZnP-V linked compound [ZnP(6)V] (Fig. 1) was synthesized as reported in the previous papers [7–10]. A zinc tetraphenyl porphyrin (ZnTPP) (Fig. 1) was also synthesized in our laboratory. The purity of ZnP(6)V and ZnTPP were confirmed by ^{1}H NMR spectra. AgPs were synthesized according to the reported procedure [3, 5]. The peak of surface plasmon due to AgP was observed at 403 nm. The average diameter of AgPs was 50 nm, as determined from transmission electron microscope (TEM) images.

The ZnP(6)V-AgP composite films with AgPs were fabricated modifying the previous method [3]. In this study, we added the step of which self-assembled monolayers (SAMs) of octanethiol (OT) were prepared by immersing an indium tin oxide (ITO) electrode (10 Ω/sq.) immobilized with AgP in an ethanol solution of OT to stabilize the absorbed AgP surface. First, the ITO-substrate was immersed into an aqueous PEI solution (0.6 mM) containing 0.2 M NaCl for 20 min at 303 K to produce an ITO-substrate modified with PEI (PEI/ITO). This positively charged ITO-electrode was then immersed into an aqueous colloidal solution of negatively-charged AgPs for 2 hours to immobilize AgPs on the positively charged ITO-electrode by the electrostatic adsorption (AgP/PEI/ITO). Next, the SAMs of OT were prepared by immersing AgP/PEI/ITO in an ethanol solution of OT to stabilize the adsorbed AgP surface, giving the AgP modified with the SAMs of OT (AgP-OT/PEI/ITO). The PEI/ITO was immersed into an ethanol solution of OT (OT/PEI/ITO). Finally, 5 μl of an ethanol solution of ZnP(6)V (0.1 mM) or a toluene solution of ZnTPP (0.2 mM) was spin-coated onto the surface of AgP-OT/PEI/ITO or OT/PEI/ITO (ZnP(6)V/AgP-OT/PEI/ITO, ZnP(6)V/OT/PEI/ITO, or ZnTPP/OT/PEI/ITO). The adsorbed amount of ZnP(6)V or ZnTPP on each substrate was evaluated from absorption spectroscopy [3]. Photocurrent measurements were carried out in an aqueous solution containing 0.1 M $NaClO_4$ using the three-electrode photoelectrochemical cell; the three electrodes were

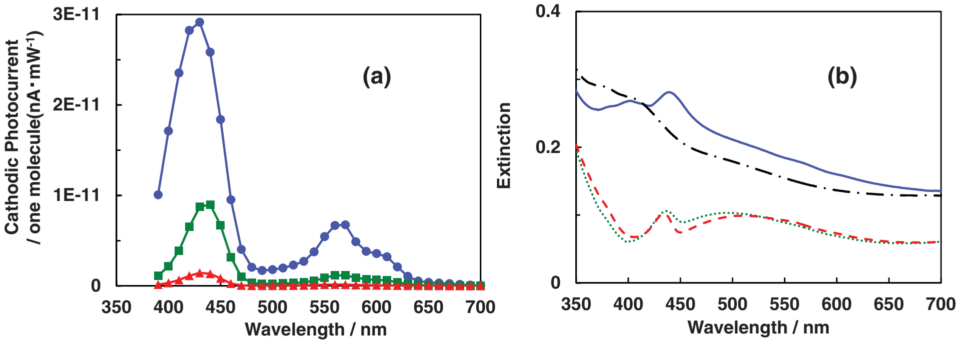

Figure 2. (a) Photocurrent action spectra of ZnP(6)V/AgP-OT/PEI/ITO (●), ZnP(6)V/OT/PEI/ITO (■), and ZnTPP/OT/PEI/ITO (▲). (b) Extinction spectra of ZnP(6)V/AgP-OT/PEI/ITO (blue unbroken line), ZnP(6)V/OT/PEI/ITO (green dotted line), ZnTPP/OT/PEI/ITO (red broken line), and AgP-OT/PEI/ITO (black dash-dotted line).

modified (working), Ag/AgCl (sat. KCl) (reference), and platinum (counter) as reported in previous paper [3]. Before measurements, oxygen bubbling was carried out for 30 min. All photocurrents were measured at $E = 0$ V versus Ag/AgCl.

Results and Discussion

In three samples, photocurrents were observed in the cathodic direction. The photocurrent action spectra of all samples (Fig. 2(a)) were in good agreement with the absorption spectra of ZnP moieties of ZnP(6)V and ZnTPP in ethanol or toluene solution or in ZnP(6)V/OT/PEI/ITO, or ZnTPP/OT/PEI/ITO (Fig. 2(b)). Therefore, it is suggested that the photocurrents are attributable to the photoexcitation of ZnP moiety. The photocurrents in ZnP(6)V/OT/PEI/ITO were larger than those in ZnTPP/OT/PEI/ITO [6 and 7 times at Soret band (430 nm) and Q band (560 nm)]. The result is ascribed by that the photoinduced electron-transfer from excited state of ZnP (ZnP^*) to V and the subsequent electron-transfer from reduced V to the oxygen in the electrolyte solution occur in ZnP(6)V/OT/PEI/ITO. It is noteworthy that the photocurrents in ZnP(6)V/AgP-OT/PEI/ITO were larger than those in ZnTPP/OT/PEI/ITO [20 and 42 times at Soret band (430 nm) and Q band (560 nm)]. From Fig. 2(b), the extinction spectra of ZnP(6)V/AgP-OT/PEI/ITO and AgP-OT/PEI/ITO show the broad absorption band around 400−500 nm is assignable to the plasmon band of isolated AgPs, or the band of transverse oscillation mode of coupled particles; as well as the smaller broad bands around 600−900 nm are assignable to the plasmon band of AgP aggregates in addition to the band for longitudinal oscillation mode of coupled particles, as reported previously [3]. An absorption band around 430−460 nm is assignable to the Soret band of ZnP moiety of ZnP(6)V in ZnP(6)V/AgP-OT/PEI/ITO. The density of AgPs was estimated to be 21% by SEM images of AgP-OT/PEI/ITO (Fig. 3). The results of extinction spectra (Fig. 2(b)) are in agreement with the SEM image. Recently, we reported that the effects of AgP-density on the photocurrents were observed and the maximum enhancements [2.6 and 9 times at Soret band (430 nm) and Q band (560 nm)] of photocurrents due to LSPR of AgPs were obtained in ZnTPP–AgP composite films (AgP-density; 7–23%) [11]. Therefore, the enhancements of photocurrents due to AgPs in ZnP(6)V–AgP composite films strongly suggest that the local electric fields appearing in the vicinity of AgP surface contribute to the enhancement of photocurrent generation based on the immobilized ZnP moiety in

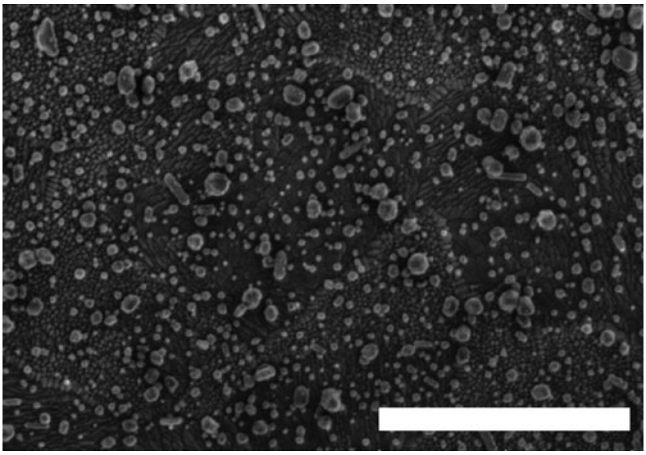

Figure 3. A SEM image of AgP-OT/PEI/ITO (scale bar = 1 μm).

ZnP(6)V. The larger enhancement of the photocurrents in ZnP(6)V–AgP composite films as compared with those in ZnTPP–AgP composite films [11] also suggests the contribution of the photoinduced intramolecular electron-transfer from ZnP* to V in ZnP(6)V–AgP composite films.

Conclusions

In this study, the large enhancement of the photocurrents in ZnP(6)V–AgP composite films as compared with those in ZnTPP films are most likely ascribed to the combination of LSPR due to AgP and photoinduced intramolecular electron-transfer from ZnP* to V in ZnP(6)V. Further investigations on the mechanism of the LSPR due to AgP on the photocurrents in donor-acceptor linked compound–AgP composite films are now in progress.

Acknowledgments

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