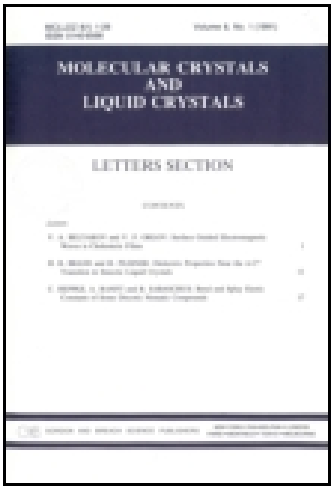

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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

Ryuji Matsumoto[a], Sunao Yamada[b] & Hiroaki Yonemura[b]
[a] Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan
[b] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan
Published online: 17 Nov 2014.

To cite this article: Ryuji Matsumoto, Sunao Yamada & Hiroaki Yonemura (2014) Effects of Gold Nanoparticles on Photocurrents of Zinc-Porphyrin-Viologen Linked Compound-Gold Nanoparticle Composite Films, Molecular Crystals and Liquid Crystals, 598:1, 86-91, DOI: 10.1080/15421406.2014.933302

To link to this article: http://dx.doi.org/10.1080/15421406.2014.933302

Mol. Cryst. Liq. Cryst., Vol. 598: pp. 86–91, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.933302

Taylor & Francis
Taylor & Francis Group

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

RYUJI MATSUMOTO,[1] SUNAO YAMADA,[2] AND HIROAKI YONEMURA[2,*]

[1]Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan
[2]Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Nishi-ku, Fukuoka, Japan

The fabrication of a zinc-porphyrin(ZnP)-viologen(V) linked compound with six methylene group (ZnP(6)V)–gold nanoparticle (AuP) composite films on indium-tin-oxide (ITO) electrodes were performed by the electrostatic layer-by-layer adsorption technique. The photocurrents in ZnP(6)V–AuP 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–AuP composite films are most likely attributable to the combination of localized surface plasmon resonance due to AuP and photoinduced intramolecular electron-transfer due to the V moiety in the linked compound.

Keywords gold nanoparticle; localized surface plasmon resonance; photocurrent; zinc-porphyrin; viologen; intramolecular electron-transfer

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 [1–9].

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 [3,6–10]. Recently, we found the remarkable enhancement of photocurrent responses based on the

*Address correspondence to Hiroaki Yonemura, Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. Tel.: +81-92-802-2814; Fax: +81-92-802-2815. E-mail: yonemura@mail.cstm.kyushu-u.ac.jp

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

photoexcitation of a tetraphenyl porphyrin, a zinc-tetraphenyl porphyrin (ZnTPP), 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 [3,6–10]. Previously, we fabricated the electrodes modified by self-assembled monolayers (SAMs) of dye compounds on the surface of the films of gold nanoparticle (AuP) aggregates, which were prepared using liquid/liquid interface [11]. We found the enhancement of photocurrents due to LSPR in organic dye–AuP aggregate films [2,4]. However, effects of AuPs on photocurrent of organic dye–AuP composite films using a donor-acceptor linked compound as an organic dye have not been elucidated yet.

In this study, we examined the effects of enhanced electric fields resulting from LSPR on the photcurrents of donor-acceptor linked compound–AuP 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 AuPs.

Experimental

Poly(ethyleneimine) (PEI, Mw = 50,000–1100,000, Wako), octanethiol (OT, TCI), and other chemicals were used as received. Amphiphilic ZnP-V linked compound [ZnP(6)V] (Fig. 1(a)) was synthesized as reported in the previous papers [12–15]. A zinc tetraphenyl porphyrin (ZnTPP) (Fig. 1(a)) was also synthesized in our laboratory. The purity of ZnP(6)V and ZnTPP were confirmed by ^{1}H NMR spectra and elemental analysis. The colloidal aqueous solution of AuPs capped with citrate was prepared by the reduction of $HAuCl_4$ with trisodium citrate according to the reported procedure [16]. The peak of surface plasmon due to AuP was observed at 533 nm. The average diameter of AuPs was 50 nm, as determined from transmission electron microscope (TEM) images.

The ZnP(6)V–AuP composite films with AuPs were fabricated modifying the previous method [3]. In this study, we added the step of which SAMs of OT were prepared by immersing an indium tin oxide (ITO) electrode (10 Ω/sq.) immobilized with AuP in an ethanol solution of OT to form the hydrophobic surface of AuP [8–10]. The fabrication procedure of ZnP(6)V–AuP, ZnP(6)V, or ZnTPP composite films on the ITO electrode is shown in Fig. 1(b). First, the ITO-electrode 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-electrode modified with PEI (PEI/ITO). This positively charged ITO-electrode was then immersed into an aqueous colloidal solution of negatively-charged AuPs for 12 hours to immobilize AuPs on the positively charged ITO-electrode by the electrostatic adsorption (AuP/PEI/ITO). Next, the SAMs of OT were prepared by immersing AuP/PEI/ITO in an ethanol solution of OT to form the hydrophobic surface of AuP, giving the AuP modified with the SAMs of OT (AuP-OT/PEI/ITO). The PEI/ITO was also 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 (0.15 mM) was spin-coated onto the surface of AuP-OT/PEI/ITO or OT/PEI/ITO (ZnP(6)V/AuP-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 electrode was evaluated from absorption spectroscopy [3,8–10]. 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 modified (working), Ag/AgCl (sat. KCl) (reference), and platinum

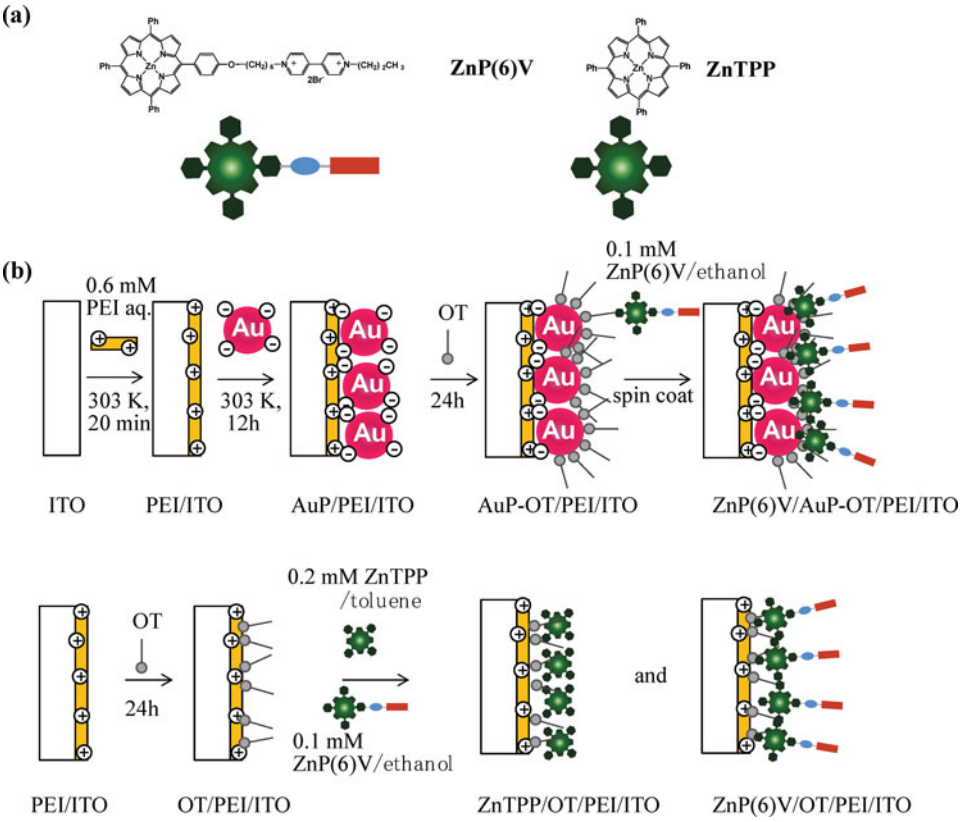

Figure 1. (a) Molecular Structures of a zinc-porphyrin-viologen linked compound with six methylene group (ZnP(6)V) and a zinc tetraphenyl porphyrin (ZnTPP) as a reference compound. (b) Schematic illustration for the fabrication of ZnP(6)V–AuP, ZnP(6)V, or ZnTPP composite films on the ITO electrode (ZnP(6)V/AuP-OT/PEI/ITO, ZnP(6)V/OT/PEI/ITO, or ZnTPP/OT/PEI/ITO).

(counter) as reported in previous paper [3,8–10]. 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 [2.2 and 2.5 times at Soret band (430 nm) and Q band (570 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/AuP-OT/PEI/ITO were larger than those in ZnTPP/OT/PEI/ITO [4.3 and 26.4 times at Soret band (430 nm) and Q band

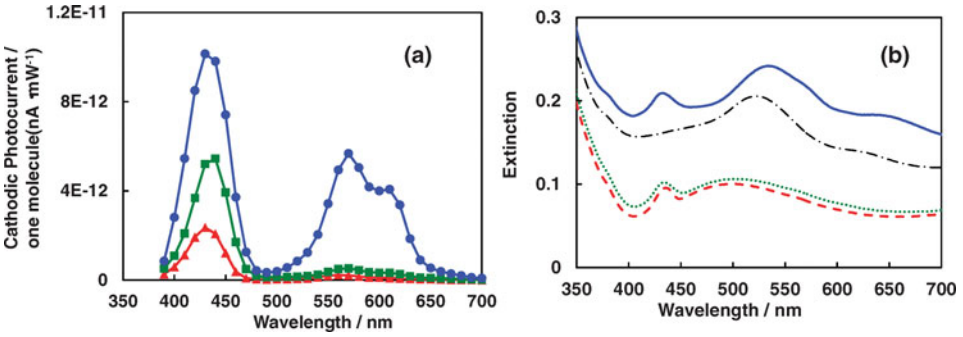

Figure 2. (a) Photocurrent action spectra of ZnP(6)V/AuP-OT/PEI/ITO (●), ZnP(6)V/OT/PEI/ITO(■), and ZnTPP/OT/PEI/ITO (▲). (b) Extinction spectra of ZnP(6)V/AuP-OT/PEI/ITO (blue unbroken line), ZnP(6)V/OT/PEI/ITO (green dotted line), ZnTPP/OT/PEI/ITO (red broken line), and AuP-OT/PEI/ITO (black dash-dotted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

(570 nm)]. From Fig. 2(b), the extinction spectra of ZnP(6)V/AuP-OT/PEI/ITO and AuP-OT/PEI/ITO show the broad absorption band around 480−600 nm is assignable to the plasmon band of isolated AuPs, or the band of transverse oscillation mode of coupled particles; as well as the smaller broad bands around 600−700 nm are assignable to the plasmon band of AuP aggregates in addition to the band for longitudinal oscillation mode of coupled particles, as reported previously [2,4,7]. An absorption band around 420−450 nm is assignable to the Soret band of ZnP moiety of ZnP(6)V in ZnP(6)V/AuP-OT/PEI/ITO. The density of AuPs was estimated to be 16 % by SEM images of AuP-OT/PEI/ITO (Fig. 3). The results of extinction spectra (Fig. 2(b)) are in agreement with the SEM image. The enhancements of photocurrents at Q band region were much larger than those at Soret band in ZnP(6)V/AuP-OT/PEI/ITO, while the enhancements of photocurrents at Q band region were almost same as those at Soret band in ZnP(6)V/OT/PEI/ITO (Fig. 2(a)), because the Q-band (500−700 nm) is in fair agreement with the plasmon bands of isolated and/or aggregated AuPs (Fig. 2(b)). Recently, we reported that effect of the density of AuPs on the photocurrents using the electropolymerized polythiophene−AuP composite ITO-electrodes were observed and the maximum enhancement (ca. 1.5 times) of photocurrents in the presence of AuP (density: 14%) was obtained [7]. We also reported

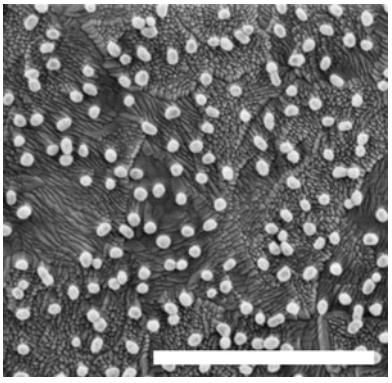

Figure 3. A SEM image of AuP-OT/PEI/ITO (scale bar = 1 μm).

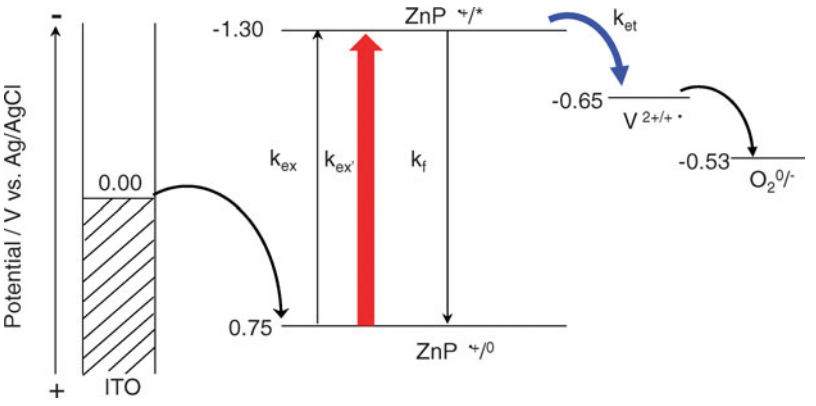

Figure 4. Schematic presentation of reaction scheme of photoelectrochemical reactions in ZnP(6)V/AuP-OT/PEI/ITO. k_{et}: rate constant of photoinduced electron-transfer from the singlet excited state of ZnP (ZnP*) to V, k_{ex}: rate constant of excitation of ZnP, k_{ex}': rate constant of excitation of ZnP in the presence of AuP (LSPR enhanced excitation), k_f: rate constant of fluorescence emission process of ZnP*.

the enhancement (ca. 10 times at 560 nm) of photocurrents due to LSPR in porphyrin compound−AuP aggregate films using SAMs [2]. Therefore, the large enhancements of photocurrents due to AuPs at Q band region (500−700 nm) in ZnP(6)V–AuP composite films strongly suggest that the local electric fields appearing in the vicinity of AuP surface contribute to the enhancement of photocurrent generation based on the immobilized ZnP moiety in ZnP(6)V (Fig. 4). The larger enhancement of the photocurrents in ZnP(6)V–AuP composite films as compared with those in ZnTPP–AuP composite films also suggests the contribution of the photoinduced intramolecular electron-transfer (k_{et}) from the singlet excited state of ZnP (ZnP*) to V in ZnP(6)V–AuP composite films as shown in the reaction scheme (Fig. 4) [10].

Conclusions

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

Acknowledgments

The authors thank the Center of Advanced Instrumental Analysis, Kyushu University and Professor Nobuo Kimizuka (Kyushu University) for performing SEM and TEM measurements, respectively. The present study was supported by Grants-in-Aid for Scientific Research (No. 25600006, No. 24651145) and Nanotechnology Network Project (Kyushu-area Nanotechnology Network) from MEXT of Japan.

References

[1] Atwater, H. A., & Polman, A. (2010). *Nat. Mater.*, *9*, 205.

[2] Akiyama, T., Nakada, M., Terasaki, N., & Yamada, S. (2006). *Chem. Commun.*, 395.
[3] Arakawa, T., Munaoka, T., Akiyama, T., & Yamada, S. (2009). *J. Phys. Chem. C*, *113*, 11830.
[4] Sugawa, K., Akiyama, T., Kawazumi, H., & Yamada, S. (2009). *Langmuir*, *25*, 3887.
[5] Akiyama, T., Aiba, K., Hoashi, K., Wang, M., Sugawa, K., & Yamada, S. (2010). *Chem. Commun.*, *46*, 306.
[6] You, J., Takahashi, Y., Yonemura, H., Akiyama, T., & Yamada, S. (2012). *Jpn. J. Appl. Phys.*, *51*, 02BK04.
[7] Takahashi, Y., Taura, S., Akiyama, T., & Yamada, S. (2012). *Langmuir*, *28*, 9155.
[8] Matsumoto, R., Yonemura, H., & Yamada, S. (2013). *J. Phys. Chem. C*, *117*, 2486.
[9] Matsumoto, R., Yamada, S., & Yonemura, H. (2013). *Jpn. J. Appl. Phys.*, *52*, 04CK07.
[10] Matsumoto, R., Yamada, S., & Yonemura, H. (2013). *Mol. Cryst. Liq. Cryst.*, *579*, 115.
[11] Suzuki, M., Niidome, Y., Terasaki, N., Kuwahara, Y., & Yamada, S. (2004). *Jpn. J. Appl. Phys.*, *43*, L554.
[12] Yonemura, H., Tahara, H., Ohishi, K., Iida, S., & Yamada, S. (2010). *Jpn. J. Appl. Phys.*, *49*, 01AD04.
[13] Tahara, H., Yonemura, H., Harada, S., & Yamada, S. (2011). *Mol. Cryst. Liq. Cryst.*, *539*, 121.
[14] Tahara, H., Yonemura, H., Harada, S., & Yamada, S. (2011). *Jpn. J. Appl. Phys.*, *50*, 081605.
[15] Tahara, H., Yonemura, H., Nakashima, A., & Yamada, S. (2012). *Chem. Phys. Lett.*, *524*, 42.
[16] Turkevich, J., Stevenson, P. C., & Hillier, J., (1951). *Discuss. Faraday Soc. 11*, 55.