

Communication

An Electrochemical Approach for Fabricating Organic Thin Film Photoelectrodes Consisting of Gold Nanoparticles and Polythiophene

Yukina Takahashi^{1,2,3}, Hidehisa Umino², Sakiko Taura² and Sunao Yamada^{1,2,3*}

¹Department of Applied Chemistry, ²Department of Materials Physics and Chemistry, ³Center for Future Chemistry, Kyushu University, Fukuoka 819-0395, Japan

ABSTRACT : A novel method of fabricating polythiophene-gold nanoparticle composite film electrodes for photoelectric conversion is demonstrated. The method includes electrodeposition of gold and electropolymerization of 2,2'-bithiophene onto an indium-tin-oxide (ITO) electrode. First, electrodeposition of gold onto the ITO electrode was carried out with various repetition times of pulsed applied potential (0.25 s at -2.0 V vs. Ag/AgCl) in an aqueous solution of HAuCl₄. Significant progress of the number density of deposited gold nanoparticles was confirmed from scanning electron micrographs, from 4 (1 time) to 25% (15 times). Next, electropolymerization of 2,2'-bithiophene onto the above ITO electrode was performed under controlled charge condition (+1.4 V vs. Ag wire, 15 mC/cm²). Structural characterization of as-fabricated films were carried out by spectroscopic and electron micrographic methods. Photocurrent responses from the sample film electrodes were investigated in the presence of electron acceptors (methyl viologen and oxygen). Photocurrent intensities increased with increasing the density of deposited gold nanoparticles up to ~10%, and tended to decrease above it. It suggests that the surplus gold nanoparticles exhibit quenching effects rather than enhancement effects based on localized electric fields induced by surface plasmon resonance of the deposited gold nanoparticles.

Organic thin film solar cells are fascinating candidates for next-generation renewable energy sources because

*To whom correspondence should be addressed.
E-mail: yamada@mail.cstm.kyushu-u.ac.jp

of their potential advantages, such as lightness of weight, easiness for processability, flexibility, and so on.¹⁻⁵ However, the future success in organic solar cells will require significant advances in materials research and concepts of cell design, thus there is still considerable room for improving the performance, while reducing the manufacturing. The skillful design of cell construction must be an important approach for improving the cell performance.

As to organic thin-film solar cells, polythiophene (PTh) has been widely investigated as a photoactive layer.⁶ However, the photophysical property of PTh substantially depends on film preparation process, such as the solvent and the concentration of the solution for spin coating.⁷ Recently, it was found that electropolymerization of 2,2'-bithiophene was useful for generating the PTh layer on the electrode.^{8,9} This method offers an advantage of applicability to give the insoluble PTh film a wide dimension on the electrode, although the present conversion efficiency is lower than regioregular poly(3-hexylthiophene) (rr-P3HT) most commonly used.

Meanwhile, photoelectrodes and solar cells with metal nanostructures of gold and silver have been intensively investigated.^{6,10-15} It is widely known that localized surface plasmon resonance (LSPR) of noble metal nanostructures can be applied to the enhancement of photocurrent from organic dye molecules. However, incorporation of such metal nanoparticles sometimes requires skillful surface decoration in order to appropriately deposit them onto the electrode. Vacuum deposition of the metals to electrode is an alternative approach, but sophisticated vacuum system is needed.

From these viewpoints, we have tried a simple and convenient approach for the fabrication of PTh-metal nanoparticle films on the electrode for photoelectric conversion. The method includes electrodeposition of gold and subsequent electropolymerization of

2,2'-bithiophene (BiTh). Photocurrent generation property of the resultant sample films was investigated employing a three electrode system in order to clarify the basic mechanism of near-field effects of AuNPs on the photocurrent enhancement of electropolymerized PTh.

The fabrication procedure of the sample film electrode by the combination of electrodeposition and electropolymerization is shown in Figure 1.

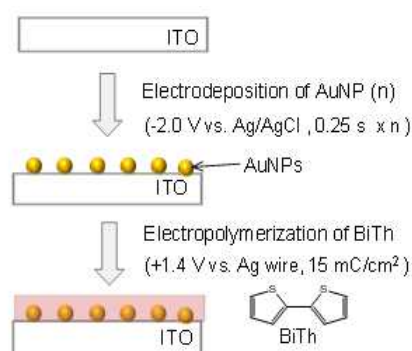


Figure 1. Procedure for fabricating PTh/AuNP(n)/ITO sample films by electrodeposition-electropolymerization process

An ITO electrode was washed with acetone, followed by ozone cleaning. Then, the ITO electrode was immersed into an aqueous solution of HAuCl_4 (0.5 g/L) as a working electrode. Reference and counter electrodes were Ag/AgCl and platinum wire, respectively. Electrodeposition of gold was carried out by serving a pulsed (0.25 s) applied voltage of -2.0 V for 1, 5, 10, and 15 times, respectively, giving the ITO electrodes with deposited gold nanoparticles, denoted as: AuNP(n)/ITO, where $n=0, 1, 5, 10,$ and 15. Electropolymerization of BiTh was also conducted in the similar procedure as above. Namely, AuNP(n)/ITO was immersed into a dichloromethane solution of BiTh (1.0 mM) and tetra (*n*-butyl)ammonium hexafluorophosphate (0.1 M as an electrolyte). Then, electropolymerization was carried out at 1.4 V and up to 15 mC/cm^2 , forming PTh on the surface of AuNP(n)/ITO. The resultant electrode was annealed at 353 K for 5 min., giving the sample electrodes denoted as: PTh/AuNP(n)/ITO ($n=0, 1, 5, 10, 15$).

Figure 2 shows the SEM images of AuNP(n)/ITO ($n=0, 1, 5, 10, 15$). Bright spots represent the resultant gold islands. It is clear that nanoparticle-like gold islands were generated on the ITO electrodes and they increased with increasing the number of pulsed electrodeposition times. Interestingly, the size and the

shape of deposited AuNPs are not so different with each other. Therefore, we evaluated the coverage of electrode with AuNPs, by assuming the generation and distribution of gold nanospheres of 16-nm diameter, without aggregation. The calculated coverage (%) with AuNPs are 4, 11, 17, and 25%, for $n = 1, 5, 10,$ and 15, respectively; as shown in the bottom of each SEM image.

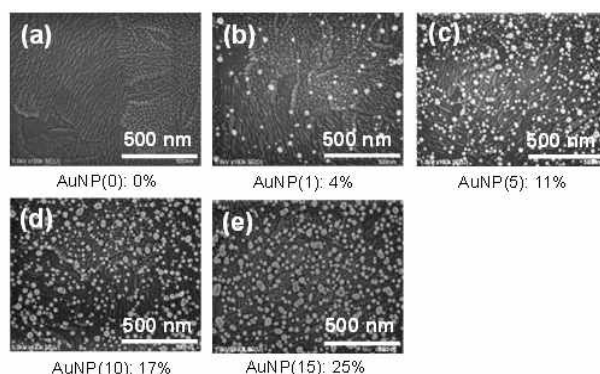


Figure 2. SEM images of AuNPs formed by electrodeposition of Au: n (number of 0.25 s-electrodeposition) = 0, 1, 5, 10, 15; denoted as AuNP(n)

We also measured the absorption spectra of AuNP(n)/ITO. In all sample electrodes, plasmon bands due to AuNPs were clearly observed around 530 nm, and they showed no appreciable shift even with the change of deposition density. These results are consistent with those of the SEM images.

Photocurrent measurements were carried out using a three electrode photoelectrochemical cell; AuNP(n)/ITO as working, Ag/AgCl as reference, and Pt wire as counter, respectively. The electrodes were fixed in the cell containing 1,1'-dimethyl-4,4'-bipyridinium dichloride (10 mM) and oxygen (bubbling with oxygen gas for 30 min.), and Na_2SO_4 (0.1 M), and PTh/AuNP(n)/ITO was irradiated with monochromatic light from the Xe lamp.

Figure 3 shows photocurrent action spectra of the sample electrodes under the identical photoirradiation condition. In the absence of AuNPs, the profile of action spectrum is quite similar to the absorption spectrum of PTh. The much lower photocurrent than rr-P3HT might be due to the random structure of electropolymerized PTh.^{9,12} Thus the photocurrent is confirmed to be induced by photoexcitation of PTh. In the presence of AuNPs, on the other hand, the maximum region of photocurrent intensity tends to show slight blue shift (around 500 nm), while the corresponding absorption spectrum show maximum region around 600 nm. It is not clear for this

discrepancy between photocurrent action profile and absorption spectrum.

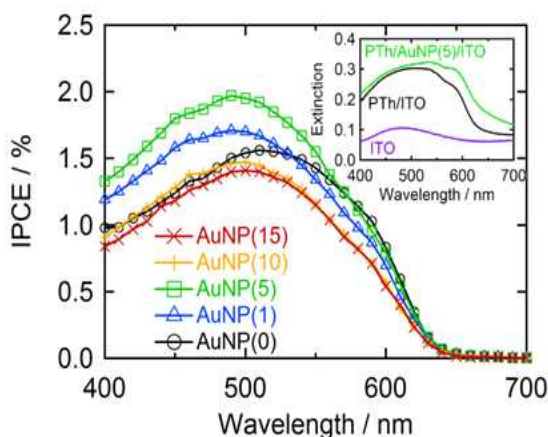


Figure 3. Incident photon-to-current conversion efficiency (IPCE) spectra of the PTh/AuNP(n)/ITO sample films fabricated by electrodeposition-electropolymerization process: n (number of 0.25 s-electrodeposition of Au) PTh electrodes with and without AuNPs.

It is also interesting that the photocurrent intensity increased with increasing the density of deposited AuNPs up to ~10%, and then tends to decrease above it. This trade-off phenomenon must be at least partially ascribed from the increased absorption of incident light with increased number of AuNPs, which also results in the relative increase of the quenching effects against saturated enhancement effects based on LSPR electric field. Accordingly, the degree of excitation of PTh with LSPR electric field will be reduced.

These results show that the optimum density of deposited AuNPs exists for overall photocurrent intensity. Similar results have been found in the case of electrostatic deposition of gold nanoparticles or silver nanoparticles onto the ITO electrode, in spite of the different formation method of organic photoabsorbing film.^{12, 16}

In conclusion, we have successfully fabricated photoresponsive films as precursor material for organic solar cells. The combination of electrodeposition and electropolymerization is very simple and convenient, and no sophisticated instruments are necessary. In addition, the PTh-AuNP films are not soluble even in organic solvents. Thus, it can be practical for use in organic solar cells, and the work is now in progress.

KEYWORDS : gold nanoparticle, electrodeposition, polythiophene, electropolymerization, photocurrents

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