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Oxidative Reaction Energy in Photopolymerization Inspired by Plasmon Induced Charge Separation

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ABSTRACT

Nanopolymerization based on plasmon induced charge separation (PICS) was performed on a gold nanoparticle (AuNP)-deposited TiO₂ substrate. Phenol and 3,4-ethylenedioxythiophene (EDOT), which have different oxidation potentials, were used as monomers. Action spectra of the polymerizations revealed that the wavelength limit of oxidation reactions based on PICS depended on the monomer. It should be caused by the different oxidation potentials of monomers. From these results, a possible mechanism of the generation of oxidation power on the metal nanoparticle based on PICS was proposed: originating from pulling down the Fermi level according to the photon energy of irradiating light.

INTRODUCTION

Metal nanoparticles, such as gold and silver ones, exhibit strong interaction with photon due to localized surface plasmon resonance (LSPR).¹ They are useful for improving the conversion efficiencies of various photoreactions, such as photoluminescence,²⁻⁵ photocatalysts,⁶ and photoelectric conversion,^{4,5,7-9} because they can enhance both excitation and emission processes of the corresponding dyes including quantum dots. Furthermore, when the resonant light irradiates a plasmonic metal nanoparticle combined with an n-type semiconductor, such as TiO₂ or ZnO, electrons in the metal nanoparticle can transfer to the semiconductor. As a result, a couple of reduction and oxidation reactions can proceed on the surfaces of the semiconductor and the metal

nanoparticle, respectively. This phenomenon, which is called plasmon induced charge separation (PICS),^{10,11} can apply to various devices with functions of photocatalysis,^{10,12,13} photoelectric conversion,^{10,14–18} sensing,¹⁹ and multicolor photochromism.²⁰ In particular, the combination of gold nanoparticle (AuNP) and TiO₂ is the one of the most suitable systems in terms of the chemical and thermal stabilities. As the reduction and oxidation powers on the surfaces of TiO₂ and AuNP, respectively, with the visible light irradiation, the system can be utilized to visible light responsive photocatalysts. However, the detailed mechanism of PICS itself is still unclear. Although it has already been reported that the electrons from plasmonic metal nanoparticles transfer to the conduction band of TiO₂, the detail of the positive charge generated on the surface of AuNP has not been fully identified yet. We first reported that oxidative photopolymerization based on PICS could be proceeded on the surface of AuNPs which were deposited on a TiO₂ substrate.²¹ Namely, oxidative nanopolymerization of pyrrole resulted in formation of polypyrrole film with the thickness of ~5 nm on the surface of AuNPs under the plasmonic resonant condition with irradiating light. It also showed that the oxidation sites could be visualized and revealed as strongly enhanced electric field regions. The reports from Murakoshi, et al. also supported our results.²²

This can further enable verification of the detailed mechanism of PICS, especially the origin of oxidation power. Additionally, the nanopolymerization method, that is able to decorate appropriate functional polymer films with nanoscale spatio-selectively, will open up a new approach for controlling photoelectrochemical properties in nanoscale interface region, such as an integrated circuit.

In this report, we employed phenol and 3,4-ethylenedioxythiophene (EDOT) as monomers instead of pyrrole, which formed polypyrrole known as a conductive polymer, and was used in the previous report.²¹ Phenol and EDOT were expected to form poly(phenol) which is known as an

insulating polymer and poly(3,4-ethylenedioxythiophene) (PEDOT) as a conductive polymer generally used for hole transport material of organic solar cells, respectively. Photopolymerization reactions of phenol and EDOT based on PICS were carefully investigated by using AuNP-TiO₂ system, and their oxidation reaction properties were compared.

EXPERIMENTAL

A TiO₂ substrate on a glass substrate was prepared by a spray pyrolysis technique from precursor solution of TiO₂ consisting of 2-propanol containing 0.3 M titanium diisopropoxide bis(acetylacetonate) with 0.15 MPa nitrogen gas for 1 s $\times$ 5 times with each 60 s interval at 550 °C and further annealing at 550 °C for 30 min in order to obtain TiO₂ substrate with a smooth surface. After UV irradiation (ca. 50 mW cm⁻²; USH-500D, Ushio, Inc.) for 1 h as pretreatment, AuNPs were photocatalytically deposited on the TiO₂ substrate from an aqueous solution containing ethanol (water/ethanol (v/v) = 3:2) and 0.4 mM HAuCl₄ with UV irradiation (ca. 50 mW cm⁻²) for 20 min.²¹ For control experiment, AuNPs were cathodically electrodeposited on an indium tin oxide (ITO)-coated glass substrate from 0.24 mM HAuCl₄ aqueous solution with the condition of -1.4 V vs. Ag|AgCl for 25 s $\times$ 5 times by using a digital potentiostat (CompactStat, Ivium Technologies) with a Ag|AgCl and a Pt wire as a reference and a counter electrodes, respectively.

Nanopolymerization was carried out in an aqueous solution containing 10 mM pyrrole or phenol, or a CH₂Cl₂ solution containing 10 mM EDOT with monochromatic light irradiation (5.0×10^{15} photons cm⁻² s⁻¹ unless otherwise noted; SM-25VE, Bunkoukeiki Co., Ltd.). UV-vis-NIR spectra (V-670, JASCO), FE-SEM (SU8000, HITACHI High-Technologies), and Raman spectra (LabRAM ARAMIS, HORIBA, Ltd.) were also carried out for characterization of the obtained polymers. Substrates were rinsed thoroughly with each solvent and dried before measurements.

RESULTS AND DISCUSSION

Nanopolymerization based on PICS

We have developed site-selective nanopolymerization method of pyrrole on the surface of AuNPs based on PICS that occurred at the interface of AuNP and TiO₂ with the irradiation of visible to near infrared light.²¹ Furthermore, we also confirmed that the size of AuNP promoting the polymerization was determined by the wavelength of the incident light, as was judged from SEM measurements of the AuNP-deposited TiO₂ substrates after light irradiation with the different wavelengths in an aqueous solution containing 10 mM pyrrole (Fig. 1). The result supported that AuNPs with various sizes on TiO₂ can produce oxidation reactions based on PICS according with the wavelength of the incident light. From this viewpoint, we applied the method to other monomers, phenol and EDOT, in this study.

First, a AuNP-deposited TiO₂ substrate was immersed into the solution containing each monomer and irradiated with the visible light. As a result, it was found that the extinction of both substrates increased after the irradiation from UV-vis-NIR spectra (Fig. 2). It indicated that the polymerization reactions of monomers might proceed. As control experiments, we confirmed that the increments of extinction were not observed without monomers, TiO₂, AuNPs, nor light irradiation. It was also confirmed by means of Raman spectra^{23,24} that each increment of extinction resulted from the generation of poly(phenol) and poly(3,4-ethylenedioxythiophene) (PEDOT), respectively (Fig. S1). SEM measurements also clarified that the polymerization proceeded site-selectively on the surfaces of AuNPs (Fig. S2), as in the case of pyrrole reported previously.²¹

Action spectra of the photopolymerization of phenol and EDOT

We examined action spectra of the photopolymerization reactions of phenol and EDOT. With proceeding of polymerization, the extinction peaks of AuNP-deposited substrates showed red-shift because the polymers increases the refractive index around the AuNPs. Furthermore, the extinction also increases because polymers have broad absorption in the visible region. It means that the increment of the extinction spectrum of the substrate with proceeding irradiation should be proportional to the amount of the polymerization. Thus, we investigated wavelength dependencies of the photopolymerization reactions by plotting the increment of the extinction peak of the AuNP-deposited TiO₂ substrates after each irradiation of monochromatic light. As results, the peaks of action spectra were well accordance with the extinction peak of AuNPs in both cases (Fig. 3). These results supported the polymerization reactions based on PICS. From Raman spectral measurements, it was verified that each wavelength limit of the polymerization reaction was approximately 1200 and 900 nm for phenol and EDOT, respectively (Fig. S3). In our previous paper,²¹ it was reported that the wavelength limit of pyrrole was approximately 1000 nm. Accordingly, it revealed that the wavelength limit of polymerization reactions based on PICS should depend on the monomer. It can be an innovative approach to control of photoelectrochemical properties in nanoscale, because various polymers which have different conductivities and optical properties can be placed site-selectively in appropriate nanospaces only by irradiating light with different wavelengths.

Discussion about the oxidizability based on PICS in this system

Many researchers have investigated mechanism of PICS.^{25,26} However, the detail theory, especially oxidation power generated by PICS, is still divided. The wavelength limits of the polymerization reactions in this study indicate that the oxidation power based on PICS should be determined by photon energy of the incident light (Fig. 4). According to literatures, the oxidative

polymerization potential of phenol, pyrrole, and EDOT are +0.89 V,²⁷ +1.34 V,²⁸ and +1.79 V vs. SHE,²⁹ respectively. It means that phenol can be polymerized with the smallest oxidative energy among the above monomer molecules. In contrast, the polymerization of EDOT requires the largest energy. These facts are well agreed with the order of the wavelength limit or photon energy which can proceed the polymerization reactions. Oxidizability based on PICS has been explained by various theories,^{26,30,31} such as generation of hole, unstable oxide on the surface of the metal nanoparticle, metal ionization, electrostatically positive charging, and positive shift of the Fermi level. SEM images in Fig. S2 revealed that the polymerization reaction proceeded all surface of the resonant AuNPs. It indicated that generation of localized positive charge, such as hot-hole and unstable oxide, should not be a dominant mechanism for the photopolymerization in this case.³² Figure 1c also supported that the photopolymerization was induced not by the total photon energy but by the energy of each photon of the irradiation light because it revealed that the polymerization reaction proceeded only on the resonant AuNP. In our system, it was reasonable explanation that the positive shift of the Fermi level of AuNP, which is corresponding to the photon energy of the incident light, occurs with transferring electrons from AuNP to conduction band of TiO₂ under illumination. Consequently, we obtained interesting results that the oxidation power based on PICS should be determined by absorbed photon energy of a metal nanoparticle, although the reduction power should be determined by the conduction band of an n-type semiconductor.

CONCLUSIONS

We succeeded in site-selective nanoscale photopolymerization of phenol and EDOT, of which polymers are expected to exhibit different photoelectrochemical properties, on the surface of the AuNP-deposited TiO₂ substrate with visible to near-IR light irradiation. It was revealed that the

wavelength limit of the polymerization reaction depended on the monomers. The results proposed that the oxidation power generated on the AuNP by PICS was determined by the photon energy of the absorption light of the AuNP. Accordingly, the oxidation power based on PICS can be explained by the positive shift of the Fermi level of the AuNP in the PICS system.

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at <https://pubs.acs.org/>

Raman spectra and SEM images of AuNP-deposited TiO₂ substrates after monochromatic light irradiation in the solutions containing phenol or EDOT.

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Fig. 1

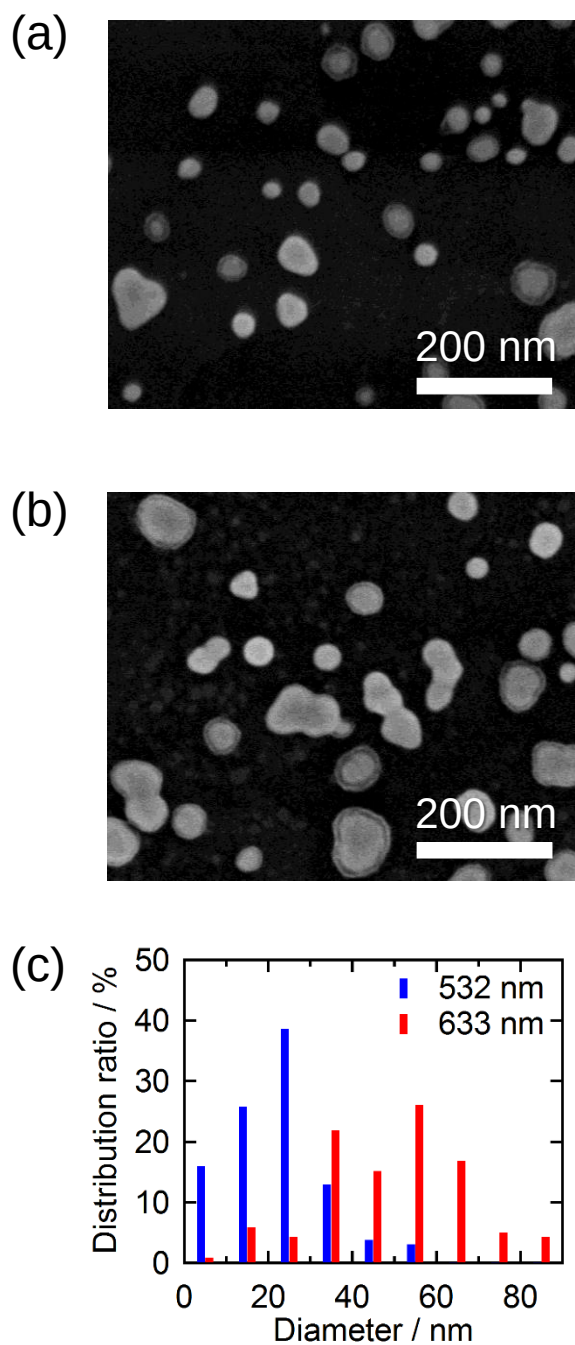


Figure 1. SEM images of the AuNP-deposited TiO₂ substrates after light irradiation with the wavelengths of (a) 532 nm (1.63×10^{16} photons cm⁻² s⁻¹) and (b) 633 nm (1.19×10^{16} photons cm⁻² s⁻¹) for 24 h in an aqueous solution containing 10 mM pyrrole. (c) The size distributions of AuNP

where polypyrrole ring was generated on after light irradiation with the wavelength of 532 (blue) and 633 nm (red).

Fig. 2

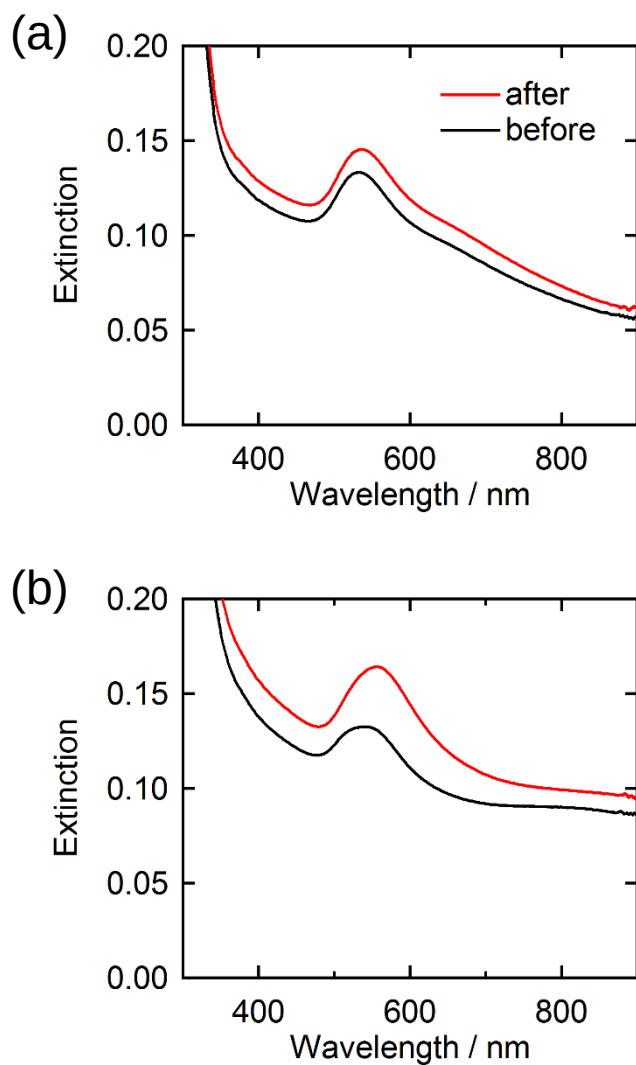


Figure 2. Extinction spectra of AuNP-deposited TiO₂ substrates in air before (black line) and after irradiation (red line) with the wavelength of 560 nm (a) in an aqueous solution containing 10 mM phenol for 18 h and (b) in a CH₂Cl₂ solution containing 10 mM EDOT for 24 h. Substrates were rinsed thoroughly with each solvent and dried before measurements.

Fig. 3

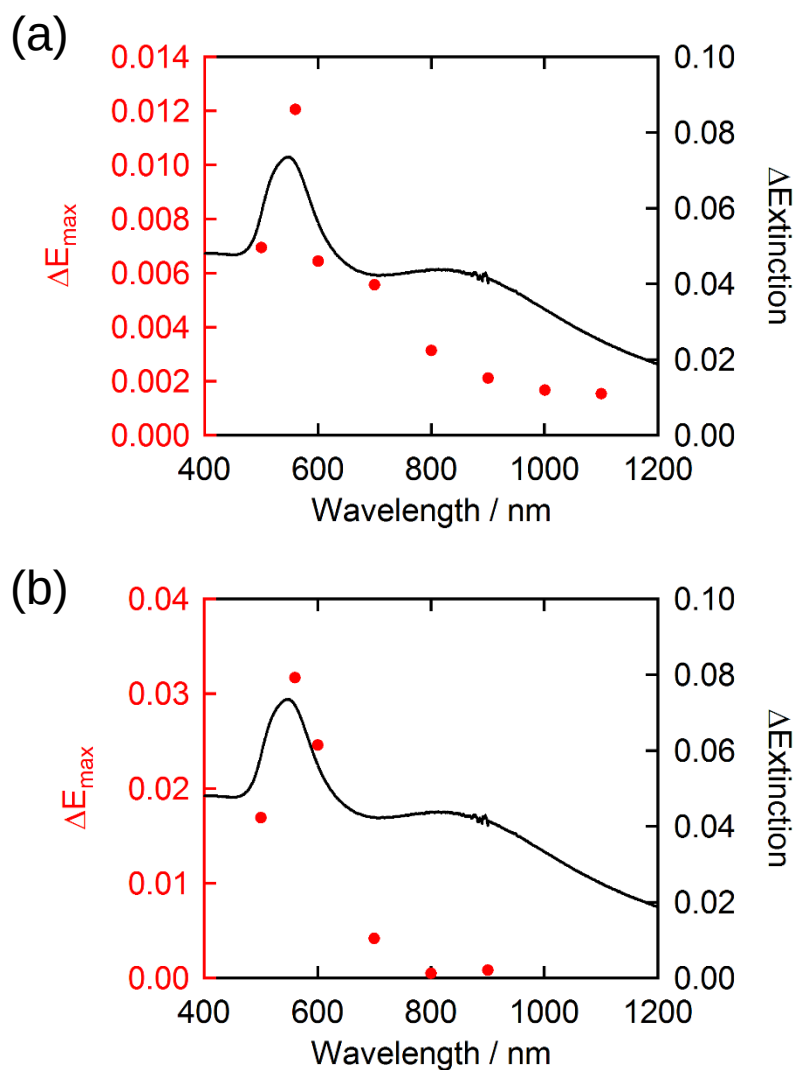


Figure 3. Action spectra of the polymerizations of (a) phenol and (b) EDOT. Extinction spectra of AuNPs on a TiO_2 substrate and the increment of the extinction peak intensities ($\Delta E_{\max}$) of AuNP-deposited TiO_2 substrates after monochromatic light irradiation ($5.0 \times 10^{15} \text{ photons cm}^{-2} \text{ s}^{-1}$) in each solutions containing phenol and EDOT for 18 h and 24 h, respectively.

Fig. 4

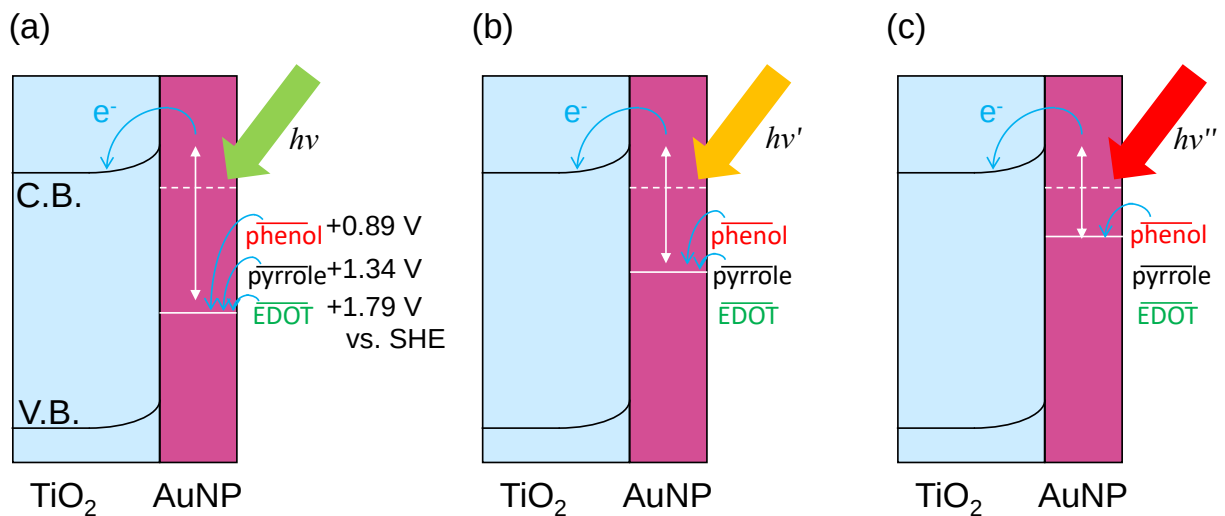


Figure 4. Proposed mechanism of the oxidation power generated on the surface of AuNP based on PICS when irradiated by the light with different wavelengths ((a) $\lambda \leq 900$ nm, (b) $900 < \lambda \leq 1000$ nm, (c) $\lambda \geq 1100$ nm).

TOC

