Gold nanoparticles-enhanced photocurrent at a dye-sensitized liquid|liquid interface

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ABSTRACT

Heterogeneous photoinduced electron transfer between a hydrophilic dye, 5,10,15,20-tetrakis(4-carboxypheny)porphyrinato zinc(II) (ZnTPPC^{4-}), and a lipophilic quencher, ferrocene, across the polarized water|1,2-dichloroethane interface was studied in the presence of citrate-stabilized gold nanoparticles (Au-NPs). A positive photocurrent arising from the photoreduction of ZnTPPC^{4-} was significantly enhanced by adding Au-NPs. The photocurrent enhancement was dependent on the concentration of Au-NPs, the excitation wavelength, and the polarization angle of the excitation light, respectively. The results demonstrated that Au-NPs act as effective photoreaction catalysts at the liquid|liquid interface.

1. Introduction

Metal and semiconductor nanoparticles are widely used to modify solid electrodes. In particular, gold nanoparticles (Au-NPs) have been studied extensively for the plasmonics application [1-3]. Under the photoexcitation at the wavelength where resonance occurs, the localized surface plasmon resonance (LSPR) and surface plasmon resonance (SPR) effects take place, respectively, for individual Au-NPs and a surface layer. In order to obtain SPR, a strict optical alignment of the photo-irradiation on surface layer should be achieved at a given wavelength. In contrast, LSPR occurs even in colloidal solution state or dispersed particles on the substrate, although the plasmon intensity is smaller than SPR. The plasmon field of Au-NPs drastically enhances the photoexcitation yield of adjacent dyes, and it has been applied to photo-energy conversion, trace analysis and biomedical applications [4-7]. Su *et al.* have reported the electric field-induced assembly of mercaptosuccinic acid (MSA)-stabilized Au-NPs at the liquid|liquid interface [8]. The interfacial concentration and assembly of Au-NPs could reversibly be controlled without aggregation or decomposition by applying potentials. Their report suggests that the photoreactive characteristics of the liquid/liquid interface could be modified in the presence of Au-NPs under potentiostatic control.

Photosynthesis involving the photoreaction of chlorophyll can take place effectively *in vivo*, and a variety of artificial photosynthesis systems employing the porphyrin derivative has been examined in biomimetic vesicles, micelles, oil droplets and liquid/liquid systems [9-12]. In the case of a heterogeneous photoinduced electron transfer between hydrophilic dyes and lipophilic quenchers across a liquid|liquid interface, the hydrophile-lipophile intermediate ion pair can be formed only in the interfacial region [12]. The improvement of the photoreaction yield has been attempted by choosing an appropriate redox couple of dye and quencher. In the present work, the photocurrent response at a dye-sensitized water|1,2-dichloroethane (DCE) interface was investigated in the presence of citrate-stabilized Au-NPs.

2. Experimental Section

5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrinato zinc(II) tetrasodium salt ($Na_4ZnTPPC$) (Frontier Scientific) was dissolved in the aqueous phase and ferrocene (Fc) (Nacalai Tesque, GR, 95%) was used as a quencher in the organic pahse. The concentrations of $ZnTPPC^{4-}$ and Fc were 1.0×10^{-4} mol dm^{-3} and 1.0×10^{-3} mol dm^{-3}, respectively. The composition of the electrochemical cell is represented in **Fig. 1(a)**. Li_2SO_4 and bis(triphenylphosphoanylidene)ammonium tetrakis(4-chlorophenyl)borate (BTPPATPBCl) were used as supporting electrolytes for the aqueous and organic phases, respectively. The aqueous solutions were prepared with water purified by a Milli-Q system (Millipore Milli-Q Integral). The organic solvent, 1,2-dichloroethane (DCE), was of HPLC grade (Nacalai Tesque, 99.7 %). All other reagents were of the highest grade available. Citrate-stabilized Au-NPs were prepared by the reduction of hydrogen tetrachloroaurate(III) tetrahydrate by adding trisodium citrate in the aqueous solution. The core size of Au-NPs was an average diameter of 17±3 nm determined by analyzing the TEM image. The plasmon absorption band of Au-NPs was observed at 522 nm for a colloidal aqueous solution in agreement with the estimated particle size [13].

A three compartment spectroelectrochemical cell was used for all measurements [14]. A flat water|DCE interface with a geometrical area of 0.50 cm^2 was polarized by a four-electrode potentiostat (Hokuto Denko HA-1010mMA1). Platinum wires were used as counter electrodes in both aqueous and organic phases. The Luggin capillaries were provided for the reference electrodes (Ag/AgCl and Ag/Ag$_2$SO$_4$). The Galvani potential difference ($\Delta_o^w \phi \equiv \phi^w - \phi^o$) was estimated by taking the formal ion-transfer potential ($\Delta_o^w \phi^{o'}$) of tetramethylammonium ion as 0.160 V [15].

In the photocurrent measurements, the water|DCE interface was illuminated under total-internal reflection (TIR) with the angle of incidence of ca. 75° by a cw laser at 410 nm (Neoark TC20-4030S-2F-4.5) or 532 nm (Photop GDLM-5050L) with a half-wave Fresnel rhomb retarder. A lock-in detection of ac-photocurrent was performed at 11 Hz by a digital lock-in amplifier with an optical chopper (NF

LI5640 with 5584A) [16]. The photocurrent action spectrum was obtained by using a Xe lamp (Hamamatsu Photonics LC8-03, 150 W). The monochromatized excitation light was irradiated perpendicularly to the interface at 11 Hz and the ac-photocurrent was measured at each wavelength. All experiments were carried out in a thermostated room at 298 ± 2 K.

3. Results and Discussion

Fig. 1(b) and **(c)** shows cyclic and ac voltammograms, respectively. The formal ion transfer potential ($\Delta_o^w \phi^{\circ\prime}$) of an oxidized form of Fc, ferrocenium (Fc$^+$), was measured as $\Delta_o^w \phi^{\circ\prime}_{Fc^+}$ at 0.03 V. The ion transfer response of ZnTPPC^{4-} was not clearly observed since $\Delta_o^w \phi^{\circ\prime}_{ZnTPPC^{4-}}$ ($= -0.25$ V) is rather close to a negative edge of the potential window [17]. The admittance responses tend to be increased in the presence of Au-NPs. The increments of the admittance could be associated with an increase of the local ionic strength by the accumulation of Au-NPs [18]. **Fig. 2(a)** shows typical photocurrent transients in the presence and absence of Au-NPs as measured under the photoexcitation at 410 nm. The photocurrents increase immediately from zero to pseudo steady-state values at positive potentials. It should be noted that no photocurrent was observed in the absence of ZnTPPC^{4-}. Furthermore, the absorption or light-scattering of the excitation light by Au-NPs in the bulk aqueous phase is negligibly small under a TIR photoexcitation from the organic phase. The photoreduction of ZnTPPC^{4-} by Fc at the water|DCE interface generates a positive photocurrent, i.e., heterogeneous photoinduced electron transfer from the organic to the aqueous phases [19]:

$$\mathrm{ZnTPPC_w^{4-}} + \mathrm{Fc_o} \xrightarrow{h\nu} \mathrm{ZnTPPC_w^{5-}} + \mathrm{Fc_o^+}$$
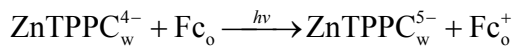
where the subscripts w and o refer to the aqueous and organic phases, respectively. The potential dependence of the photocurrent basically is correlated with the electron transfer rate constant, which is increased with increasing $\Delta_o^w \phi$ [20], and the interfacial behavior of ZnTPPC^{4-} [19]. The interfacial concentration of ZnTPPC^{4-} increases when $\Delta_o^w \phi$ approaches its transfer potential ($\Delta_o^w \phi^{\circ\prime}_{ZnTPPC^{4-}}$). At potentials close to $\Delta_o^w \phi^{\circ\prime}_{ZnTPPC^{4-}}$, however, a high interfacial concentration induces the formation of nonphotoreactive aggregates [17]. The decrement of the photocurrent at negative potentials is also inseparably connected to the ion transfer of photoproducts, i.e., the positive photocurrent could be canceled out through the instantaneous transfer of Fc$^+$ to the aqueous phase at $\Delta_o^w \phi < \Delta_o^w \phi^{\circ\prime}_{Fc^+}$. Thus, the

heterogeneous photoinduced electron transfer across the interface can effectively take place at $\Delta_o^w \phi_{Fc^+}^{o'} < \Delta_o^w \phi$ within the potential window. The photocurrent transients in the presence of Au-NPs exhibited distinct enhancements of the positive photocurrent (**Fig. 2(a)**). At $\Delta_o^w \phi^{o'} > 0.10$ V, e.g., the pseudo steady-state photocurrent (Δi_{photo}) is more than four times greater magnitude in the presence of Au-NPs. The lock-in detection of the ac-photocurrent was carried out at 11 Hz as shown **Fig. 3(a)**, and the potential dependence of the ac-photocurrent coincides with the pseudo steady-state photocurrent in **Fig. 2(b)**. In the positively polarized condition, the magnitude of the real ($i_{photo,re}$) and imaginary ($i_{photo,im}$) components was gradually increased by adding Au-NPs. A slight increase of negative $i_{photo,im}$ at higher concentrations might be associated with slow charge transfer process such as homogeneous photoreaction followed by an ion transfer of the photoproduct [16].

The structural changes of the interface such as corrugation or roughening associated with the accumulation of Au-NPs might slightly increase an effective interfacial area [18, 21]. It is, however, insufficient to explain the significant enhancement of the photocurrent observed in this study. The photocurrent enhancements in the presence of Au-NPs, thus, should be correlated with Au-NPs acting as (**case I**) sensitizers involving the localized surface plasmon (LSP) effect to improve the photoreaction yield or (**case II**) electron transfer mediators between ZnTPPC^{4-} in water and Fc in DCE. Lahtinen *et al.* have reported that Pd-NPs could act as electron transfer mediators for photocatalytic reaction at the interface [22]. The photocurrent action spectrum at 0.20 V was measured in the presence and absence of 4.9×10^{-3} g dm^{-3} Au-NPs by the lock-in detection at 11 Hz (**Fig. 3(b)**). In this case, the photocurrent responses were normalized at the irradiation power of 0.5 mW taking into account the spectral distribution of the Xe lamp. The photocurrent action spectra were well correlated with the absorption spectrum of ZnTPPC^{4-} in the aqueous phase, and a maximum photocurrent was observed around the Soret band at 420 nm. The action spectra indicate that Au-NPs enhance the photocurrent in a wide visible region. In addition, the photocurrent enhancement seems to be more effective in the Q band region close to the resonant plasmon band of Au-NPs at 522 nm, e.g., the photocurrent was 114% at 420 nm and 163% at 520 nm, respectively, in the presence of Au-NPs. The dependence of the pseudo

steady-state photocurrent on the polarization angle (Ψ) of the excitation beam was also measured under TIR conditions. Both in the presence and absence of Au-NPs, the maximum value of Δi_{photo} was obtained with the *s*-polarized excitation beam ($\Psi = 90°$) which is parallel polarization to the interfacial plane (**Fig. 3(c)**). The polarization angle dependence of the photocurrent relates to the average orientation angle (θ) of transition dipole moments of ZnTPPC^{4-} adsorbed at the interface [19]. The θ value in the absence of Au-NPs was estimated, respectively, as $66\pm3°$ at 0.20 V and $67\pm2°$ at 0.30 V with respect to the normal of the interface. The estimated θ values indicated that ZnTPPC^{4-} molecules are adsorbed nearly in parallel to the interface. In addition, the polarization angle dependence was relatively improved by adding Au-NPs, in which the ratio of the *s*- and *p*-polarized photocurrents ($\Delta i_{\text{photo}}^{\text{s}} / \Delta i_{\text{photo}}^{\text{p}}$) at 0.20 V of 1.5 was increased to 1.8 by adding Au-NPs. In principle, the LSP field is generated in parallel to the polarization of the excitation light [3, 23]. The relatively large $\Delta i_{\text{photo}}^{\text{s}} / \Delta i_{\text{photo}}^{\text{p}}$ value in the presence of Au-NPs would indicate either effective photoexcitation of ZnTPPC^{4-} oriented parallel to the interface in the *s*-polarized LSP field or orientation change of ZnTPPC^{4-} adsorbed at the interface. Although the action spectra and polarization angle dependences of the photocurrents seem to support the mechanism (**case I**) phenomenologically, a further kinetic study is essential to elucidate a detailed mechanism of the photocurrent enhancement.

4. Conclusions

The photocurrent response at the dye-sensitized water|DCE interface was effectively enhanced in the presence of Au-NPs in the aqueous phase. The photocurrent enhancement over a wide wavelength range was observed in the photocurrent action spectra. The present results clearly demonstrated that Au-NPs can be used as effective photoreaction catalysts at the polarized liquid|liquid interface.

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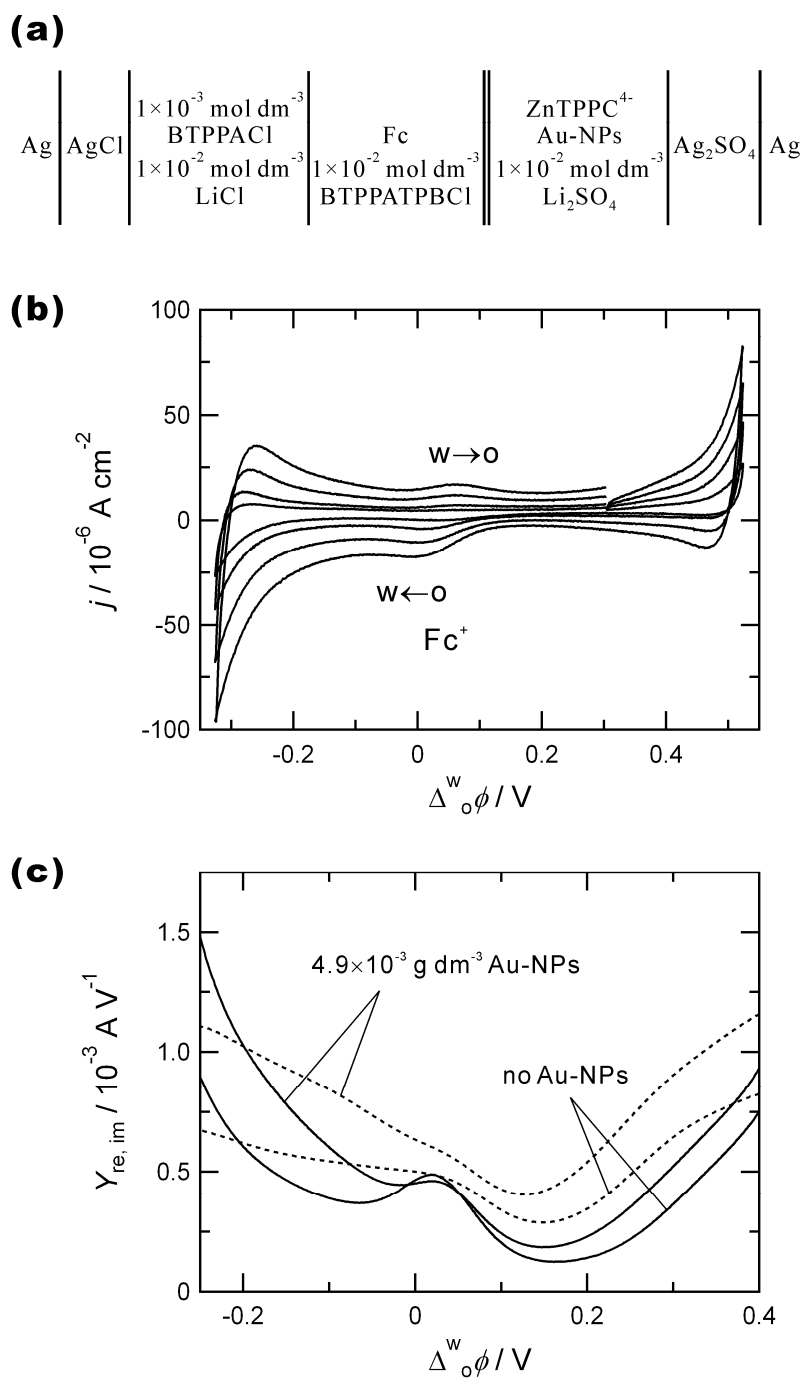[23] K.A. Willets, R.P. Van Duyne, Annu. Rev. Phys. Chem. 58 (2007) 267.

(a)

$$\text{Ag} \mid \text{AgCl} \left| \begin{array}{c} 1\times10^{-3}\ \text{mol dm}^{-3} \\ \text{BTPPACl} \\ 1\times10^{-2}\ \text{mol dm}^{-3} \\ \text{LiCl} \end{array} \right| \begin{array}{c} \text{Fc} \\ 1\times10^{-2}\ \text{mol dm}^{-3} \\ \text{BTPPATPBCl} \end{array} \left\| \begin{array}{c} \text{ZnTPPC}^{4-} \\ \text{Au-NPs} \\ 1\times10^{-2}\ \text{mol dm}^{-3} \\ \text{Li}_2\text{SO}_4 \end{array} \right| \text{Ag}_2\text{SO}_4 \mid \text{Ag}$$

(b)

(c)

Fig. 1. **(a)** Composition of the electrochemical cell, **(b)** cyclic and **(c)** ac voltammograms of the ZnTPPC^{4-}/Fc system in the presence of 4.9×10^{-3} g dm^{-3} Au-NPs in the aqueous phase. The real (Y_{re}) and imaginary components (Y_{im}) of the admittance are represented by the solid and dashed lines, respectively. The potential sweep rates were **(b)** 10, 20, 50, 100 mV s^{-1} and **(c)** 5 mV s^{-1}. The potential modulation for the admittance measurements was 10 mV at 11 Hz.
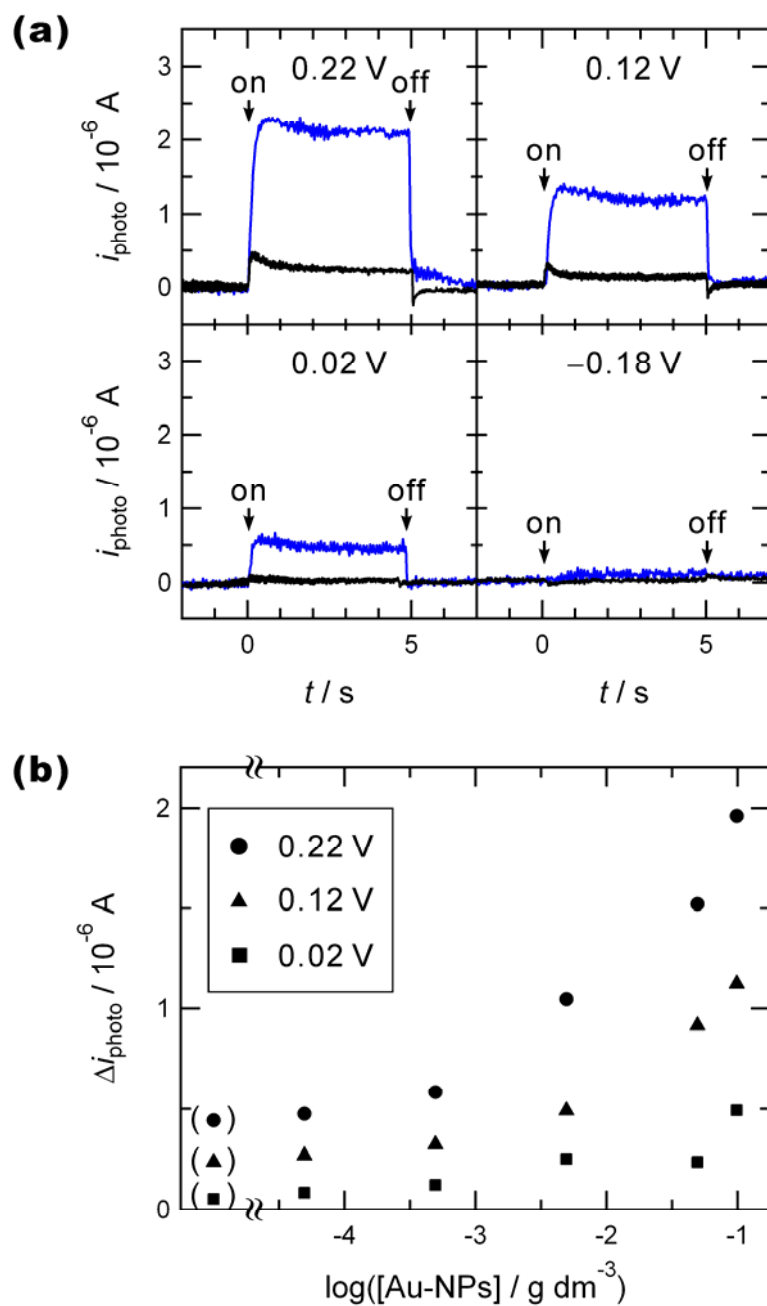
Fig. 2. **(a)** Photocurrent transients and **(b)** pseudo steady-state photocurrents (Δi_{photo}) at the water|DCE interface. The blue and black lines for the transients refer to the presence and absence of 9.9×10^{-2} g dm^{-3} Au-NPs in the aqueous phase. The excitation light source was a cw laser of 22 mW at 410 nm in TIR. The symbols in parentheses denote the photocurrent in the absence of Au-NPs.
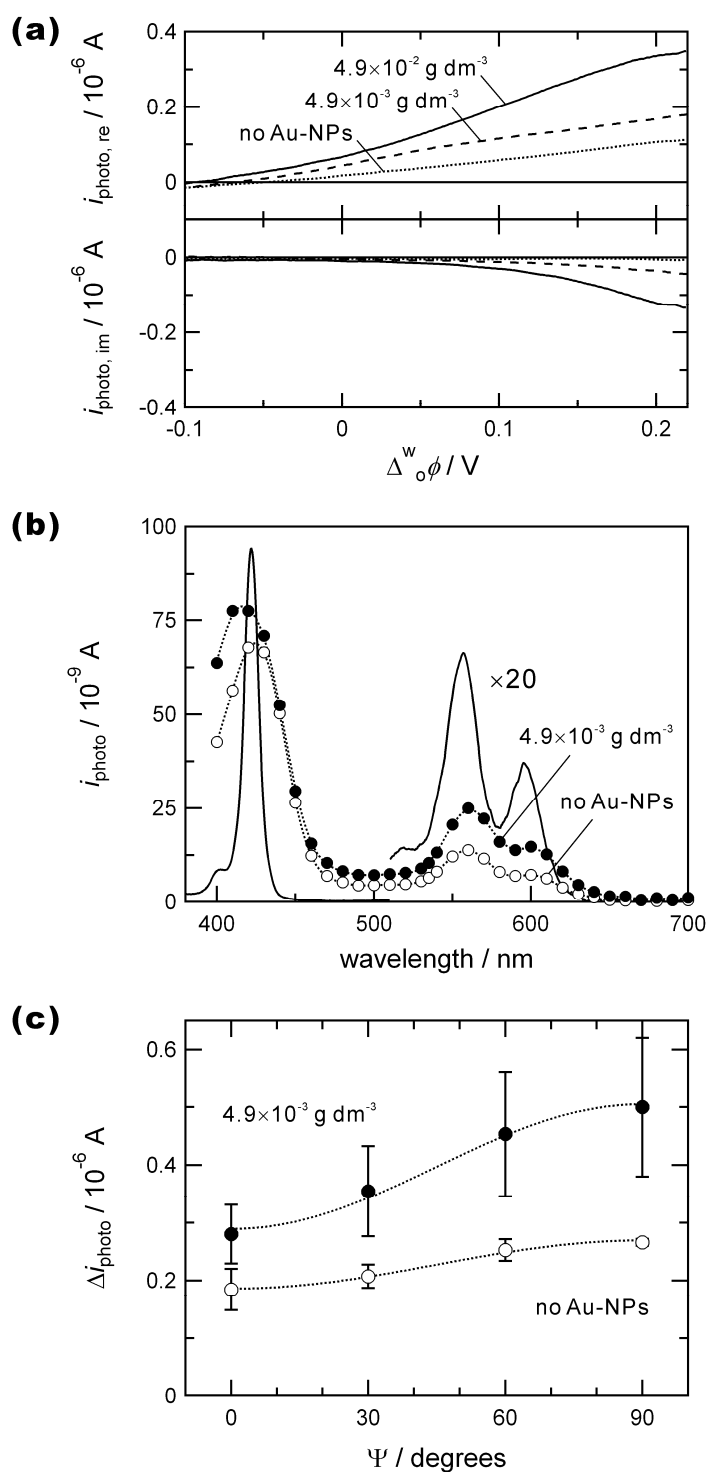
Fig. 3. (a) Potential dependence of the real ($i_{photo,re}$) and imaginary components ($i_{photo,im}$) of the ac-photocurrent at 11 Hz, **(b)** photocurrent action spectra at 0.20 V with a typical absorption spectrum of ZnTPPC^{4-} in the aqueous phase (solid line), and **(c)** dependence of pseudo steady-state photocurrents (Δi_{photo}) at 0.20 V on the polarization angle of the excitation beam (Ψ). The excitation light source was **(a)** 11 mW at 410 nm in TIR and **(b)** monochromatized Xe lamp, respectively, with frequency of 11 Hz, and **(c)** cw laser of 50 mW at 532 nm in TIR.