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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 phase. 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

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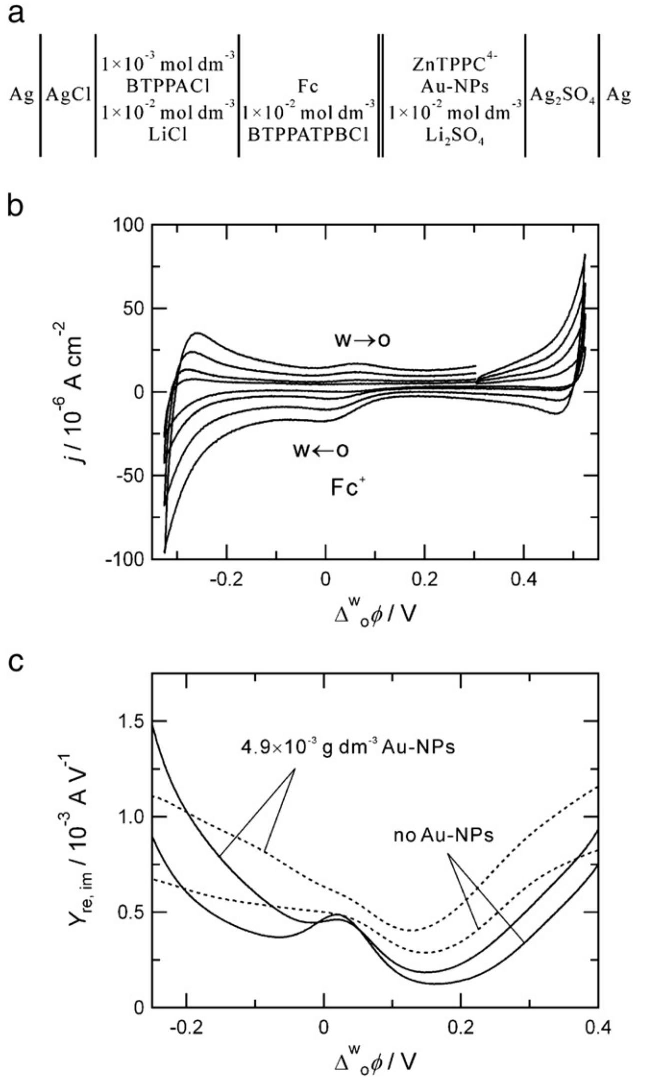

Fig. 1. (a) Composition of the electrochemical cell, (b) cyclic and (c) ac voltammograms of the $\mathrm{ZnTPPC^{4-}}$/Fc system in the presence of 4.9×10^{-3} g $\mathrm{dm^{-3}}$ Au-NPs in the aqueous phase. The real ($Y_{\rm re}$) and imaginary components ($Y_{\rm im}$) of the admittance are represented by the solid and dashed lines, respectively. The potential sweep rates were (b) 10, 20, 50, 100 mV $\mathrm{s^{-1}}$ and (c) 5 mV $\mathrm{s^{-1}}$. The potential modulation for the admittance measurements was 10 mV at 11 Hz.

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 $\mathrm{cm^2}$ 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 $\mathrm{Ag/Ag_2SO_4}$). The Galvani potential difference ($\Delta_{\rm o}^{\rm w}\phi\equiv\phi^{\rm w}-\phi^{\rm o}$) was estimated by taking the formal ion-transfer potential ($\Delta_{\rm o}^{\rm w}\phi^{\rm o\prime}$) 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 ($\Delta_{\rm o}^{\rm w}\phi^{\rm o\prime}$) of an oxidized form of Fc, ferrocenium ($\mathrm{Fc^+}$), was measured as $\Delta_{\rm o}^{\rm w}\phi_{\rm Fc^+}^{\rm o\prime}$ at 0.03 V. The ion transfer response of $\mathrm{ZnTPPC^{4-}}$ was not clearly observed since $\Delta_{\rm o}^{\rm w}\phi_{\rm ZnTPPC^{4-}}^{\rm o\prime}$(= − 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 $\mathrm{ZnTPPC^{4-}}$. 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 $\mathrm{ZnTPPC^{4-}}$ by Fc at the water|DCE interface generates a positive photocurrent, i.e.,

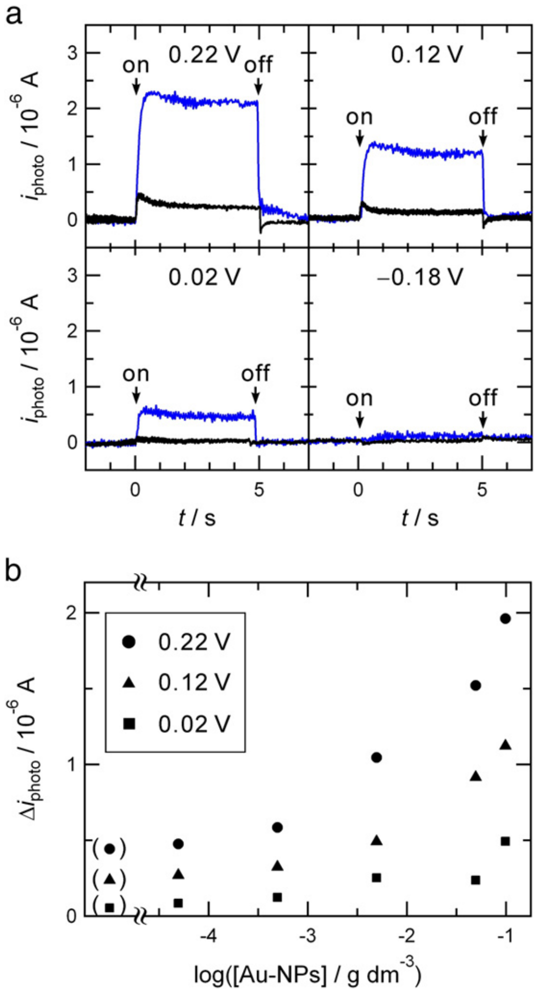

Fig. 2. (a) Photocurrent transients and (b) pseudo steady-state photocurrents ($\Delta i_{\rm photo}$) at the water|DCE interface. The blue and black lines for the transients refer to the presence and absence of 9.9×10^{-2} g $\mathrm{dm^{-3}}$ Au-NPs in the aqueous phase. The excitation light source 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.