Immobilization of Photosynthetic Reaction Center Complexes onto a Hydroquinonethiol-Modified Gold Electrode

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The immobilization of reaction center complexes onto a gold electrode was attempted through the binding affinity between reaction centers and hydroquinone-2-thiol adsorbed on an electrode surface. The largest anodic photoresponse by immobilized reaction centers was observed using ubiquinone B-depleted reaction centers and with the pre-oxidation of adsorbed hydroquinone-2-thiol, indicating that the degree of the orientation of reaction center particles increases through the binding affinity between vacant Q_B-sites in the particles and *p*-benzoquinonethiol. This anodic photoresponse could be elongated over a period of 5 h (2500 cycles of turnover number) by adding cytochrome c_2 into the electrolytic solution.

The utility of fossil fuels should be limited considering such serious environmental problems as air pollution with NO_x and SO_x, and the release of vast amounts of CO_2. Although the concept of photosynthetic solar-energy conversion through water splitting is not new, the development of solar-energy technology is still desired, while promising a substantial contribution to the growing energy demands in the future. The primary processes of photosynthesis are the most efficient for converting solar energy to chemical energy and, consequently, could possibly be used as the basis for modifying photosynthetic processes applicable to solar energy conversion.[1] Supporting this viewpoint, many studies[2] have demonstrated the possibility of employing photoactive biological components in photoelectrochemical cells, in connection with studies on the mechanism of photosynthetic primary processes as well as solar-energy conversion projects. We have also been studying the photoelectrochemical behavior of reaction center complexes at a Pt electrode immersed in the suspension;[3] a cathodic photocurrent could be observed upon illumination under potentiostatic conditions, while a negligibly small anodic photocurrent was observed even under anodic polarization. After a while, we first observed an anodic photoresponse of a reaction center suspension by means of the surface modification of a gold electrode with hydroquinone-2-thiol,[4] although the generated anodic photoresponse was still smaller than expected. An X-ray crystallographic analysis showed[5] that the reaction center particle was almost spherical in shape with an average diameter of 6 nm. If only an electron-transfer site with the electrode is assumed to be located on a particle with such a large spherical shape, the generation of such a small anodic photocurrent seems to be sufficiently reasonable. In fact, the functional position of electron-transfer components, such as bacteriochlorophyll, bacteriopheophytin, and ubiquinone 10, is tightly bound to the reaction center particle. It therefore becomes important when considering the exchange of electrons between a particle and the electrode. Thus, the small anodic photoresponse is due to the poor efficiency of electron transfer from the reaction centers to the electrode based on a structural anisotropy of the reaction center particle, as shown in Fig. 1(a). Thus, in order to enhance the anodic photocurrent, the reaction center particles should be oriented at a molecular level on the electrode surface, as shown in Fig. 1(b). The Langmuir–Blodgett technique and an affinity binding method with an avidin–biotin couple were examined for preparing a reaction center thin film.[6,7] However, the attempts were far from successful, because of a difficulty to construct organization and of an obstacle to interprotein electron transfer by voluminous avidin, respectively. It is well known[8] that ubiquinone B, which is a terminal electron acceptor in the reaction center particle, is easily extractable from the particle by treating with organic solvents or surfactants, although the capacity to perform a primary photoact was somewhat impaired. In addition, the thus-depressed electron-transfer activity could be restored to some extent by reconstituting either intrinsic ubiquinone 10 or other artificial quinones to the ubiquinone-depleted reaction centers. We report here on an enhancement of the anodic photocurrent under anodic polarization by means of the immobilization of ubiquinone B-depleted reaction center complexes onto a surface-modified gold electrode through a binding affinity between vacant Q_B-sites in the reaction center particles and hydroquinone-2-thiol on the electrode surface.

Experimental

A carotenoid- less blue- green mutant strain (G- 9) of *Rhodospirillum rubrum* was used throughout the present study. The cells were grown anaerobically at 30 °C for 3 d under continuous illumination from tungsten lamps, as described previously.[9] The subcellular photosynthetic apparatus, chromatophores, were prepared

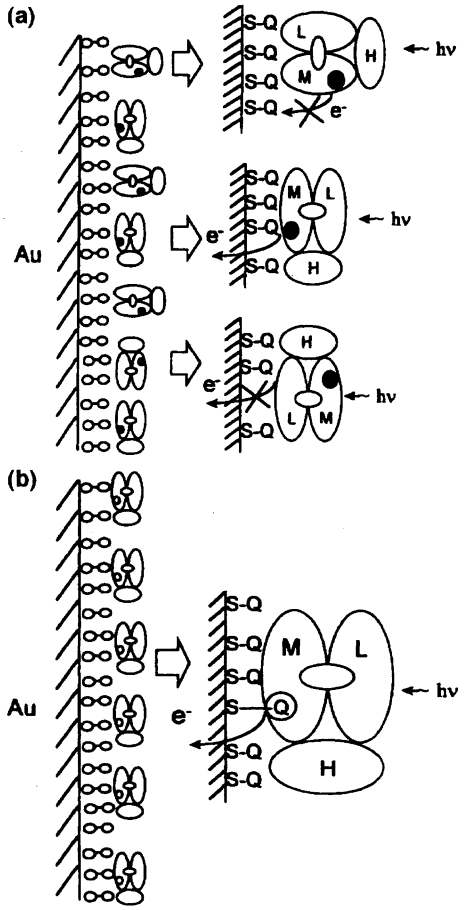

Fig. 1. Schematic representation for immobilization of native (a) or Q-depleted (b) RC onto a hydroquinonethiol-modified gold electrode.
A reaction center particle consists of three subunits, labeled as L, M, and H. An electron is ejected, in response to illumination, from a reaction center bacteriochlorophyll dimer (so-called P870, which is shown as the small open ellipse, ⬭, in the figure) to the terminal electron acceptor, ubiquinone B (also shown as the shadowed circle, ●, in the figure). Although the electron must be transferred from the reduced ubiquinone B to an electrode in order to generate the anodic photocurrent, its efficiency is very low due to such a structural anisotropy (a). So, the reaction center particles should be oriented at a particle level on the electrode surface as shown in Fig. (b). Ubiquinone B can be easily extracted from the particles (the resulting vacant site is named as the vacant Q_B-site, shown as the open circle, ○, in the figure), and some artificial quinones can be reconstituted to the vacant Q_B-site. We will examine the oriented immobilization of the reaction center particles onto a hydroquinonethiol-modified gold electrode through a binding affinity, as shown in Fig. (b).

from the light-grown cells by sonication, followed by differential centrifugation.[10] Reaction center complexes were isolated from the chromatophores with *N,N*-dimethyldodecylamine *N*-oxide (LDAO) by the method of Vadeboncoeur et al.[11] with slight modifications. The thus-prepared reaction centers were finally solubilized in 0.1 M (M = mol dm^{-3}) tris(hydroxymethyl)methanamine (Tris) buffer (pH 7.5) containing 0.025% LDAO, and stored at 4 °C in the dark. This preparation showed an absorbance ratio of 1.30 at 802 to 280 nm, indicating high purity. This purity was reconfirmed by the result of SDS-PAGE, in which no appreciable band could be found, except those assigned to the L-, M-, and H-subunits. We hereafter designate this preparation as native RC. The density of the reaction center suspension was expressed in terms of the absorbance of the bound bacteriochlorophyll at 802 nm (A_{802}, A_{802} = 1 corresponding to 3.47 μM of bacteriochlorophyll[12]). Ubiquinone B was extracted from the native RC by the method of Gimenez-Gallego et al.[13] with slight modifications, in order to increase the binding affinity of hydroquinone-2-thiol on a gold electrode to the vacant Q_B-sites in the ubiquinone B-depleted reaction centers. Thus-obtained ubiquinone B-depleted reaction centers were also suspended in the same buffer. We designate this preparation as Q-depleted RC. The quantity of ubiquinone 10 in the reaction center particle was determined by HPLC. The results showed that 1.14—1.17 molecules of ubiquinone 10 (i.e., one molecule as ubiquinone A and the remainder as ubiquinone B) were present in a Q-depleted RC particle, while 1.85—1.89 molecules of ubiquinone 10 (i.e., one molecule of ubiquinone A and nearly one molecule of ubiquinone B) were in a native RC particle. These values mean that at least 15% of the native RC particles remain in the Q-depleted RC preparation, and about 10% of the Q-depleted RC particles are contaminated in the native RC preparation.

Hydroquinone-2-thiol was synthesized by an ordinary method,[14] and modified on a gold-plate electrode (1×3 cm^2 of surface area) through the chemisorption of thiol groups by dipping the electrode for 10 min. into a 10 mM methanolic solution, followed by washing with a large excess of methanol. The redox potential of the modified hydroquinone-2-thiol was determined to be +220 mV vs. NHE in Tris buffer (pH 7.5). Since it is presumably considered that hydroquinone-2-thiol is adsorbed on the gold electrode surface as a mixture of both its oxidized and reduced forms, because of its autooxidizability, the hydroquinonethiol-modified gold plate electrode was, if necessary, pre-electrolyzed in Tris buffer (pH 7.5) at either +400 or +50 mV vs. NHE in order to completely oxidize or reduce the modified quinone. The native RC or Q-depleted RC was then immobilized on the hydroquinonethiol-modified gold plate electrode by dipping into the RC suspension (A_{802} = 1), followed by gentle, but copious, washings in the buffer.

An experimental cell[15] with a light path length of 0.4 mm comprised the RC-immobilized working electrode, a Pt foil counter electrode, and an Ag/AgCl reference electrode. All of the potentials listed in this paper were corrected against a normal hydrogen electrode (NHE) for convenience. For a potentiostatic measurement, the potential of the working electrode was controlled with a Hokuto Model potentiostat HA-501, and the resulting current was recorded. The photocurrent was measured, upon illumination, after electrolyzing in the dark at a certain potential in a Tris buffer at 25 °C. The light source was a 60 W tungsten lamp, usually using in combination with a 12 cm thick water filter in order to eliminate any thermal effects. A 500 W xenon arc lamp (Wacom Model MX-500) was used in combination with a JASCO Model CT-25N grating monochromator equipped with a cut-off filter (UV-39 or VR-69) for measuring a photocurrent action spectrum. Dissolved Oxygen was removed from the solution by bubbling argon for 30 min.

Results and Discussion

Typical current-time profiles obtained at the RC-immobilized gold electrode are shown in curves **c** and **d** of Fig. 2, together with those obtained in a RC suspension[4] (curves **a**

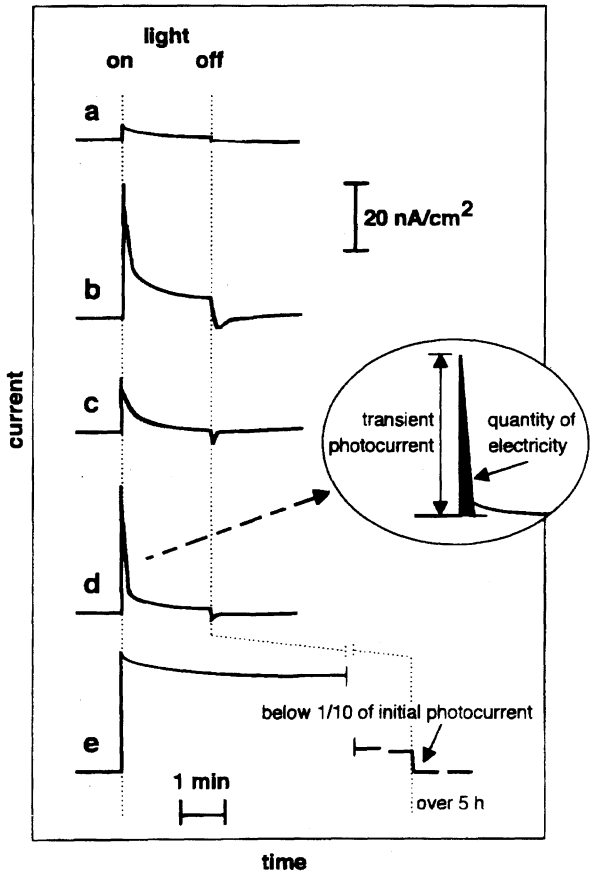

Fig. 2. Typical current-time profiles for the photocurrent generation by reaction centers.
The photocurrent was measured at +300 mV of applied potential, 6000 lx of illuminance, and 7.5 of the solution pH; (a) at the naked gold electrode in the native RC suspension (A_{802} = 1), (b) at the hydroquinonethiol-modified gold electrode in the native RC suspension (A_{802} = 1), (c) at the native RC-immobilized gold electrode (60 min. of dipping time), (d) at the Q-depleted RC-immobilized gold electrode (60 min. of dipping time), and (e) at the Q-depleted RC-immobilized gold electrode in the presence of 200 μM of the reduced form of cytochrome c_2.

and **b**) for a comparison. The increase of the current, upon illumination, was taken as the value of the transient photocurrent, and the black-shadowed portion of the insert in Fig. 2 as the value of the quantity of electricity for the anodic photoresponse. As mentioned previously,[4] a very small continuous anodic photocurrent was observed at a naked gold-plate electrode immersed in a native RC suspension under anodic polarization (curve **a**). On the other hand, at a hydroquinonethiol-modified electrode in a RC suspension, transient anodic and cathodic photocurrents were superposed on the small anodic photocurrent when light was switched on and off (curve **b**). Hirata and Miyake[16] have recently reported the site-specific binding of Q-depleted RC from *Rhodopseudomonas viridis* to the Langmuir–Blodgett film of a quinonylphospholipid, *N*-[12-(3-chloro-1,4-naphthoquinon-2-ylamino)dodecyl]dipalmitoyl-L-α-phosphatidylethanolamine, through the intrinsic affinity between vacant Q_B-site and quinonyl head group, and have suggested photoexcited electron transfer from the reaction center bacteriochlorophyll to the quinonyl moiety via menaquinone (Q_A). Because the generation of transient photocurrents therefore seems to be due to the adsorption of RC particles to the electrode surface through an affinity between the reaction center particle and hydroquinone molecule on the electrode,[4] a RC-immobilized electrode was prepared by immersing the hydroquinonethiol-modified gold electrode into the native and Q-depleted RC suspensions. Using these electrodes, transient anodic and cathodic photocurrents were again generated by turning on and off of the light (curves **c** and **d**). These pulses by Q-depleted RC were followed by rapid relaxation (curve **d**), whereas the transient photocurrent by native RC was relaxed more slowly comparing with curve **d** (curve **c**). The transient anodic photocurrent by Q-depleted RC became about 1.6-times larger than that observed in the suspension. It is widely accepted[17] that a single reaction center particle can transfer just one electron from bacteriochlorophyll to ubiquinone B in response to illumination, and that the resulting oxidized bacteriochlorophyll must be reduced again before the particle can perform another photochemical electron transfer. It thus seems probable that this characteristic photoresponse can be attributed to single charge separation in the reaction center particle. In addition, the small continuous anodic photocurrent, as those observed in the suspension, remain disappeared (curves **c** and **d**), and that by native RC has been larger than that by Q-depleted RC. When a hydroquinonethiol-modified gold electrode without any further immobilization of RC was illuminated under the same potentiostatic conditions, a continuous photocurrent was generated, although the value of the photocurrent was very small (data not shown). *p*-Benzoquinonethiol (hydroquinone-2-thiol with oxidized form) in a methanolic solution showed an absorption maximum at 435 nm and an absorption edge at about 580 nm. Moreover, the photocurrent at the hydroquinonethiol-modified electrode could not be observed with setting an R-65 cut-off filter in the light path. Thus, the generation of a residual, negligibly small photocurrent (a part of the continuous photocurrent) results from *p*-benzoquinonethiol on the electrode, although the mechanism is not clear at the present stage. The remainder seems to result from a slow electron-transfer process based on a conformation change, such as the rotation of physically adsorbed reaction center particles, not through an affinity to the hydroquinone-2-thiol molecule on the electrode.

The quantity of immobilized RC increased with increasing time of dipping up to about 60 min, as shown in Fig. 3(a). The quantity of Q-depleted RC was estimated to be 2.1×10^{12} particles cm^{-2} as a maximum value based on the quantity of electricity of the transient photocurrent, assuming that an electron is transferred upon illumination from a reaction center particle to the electrode. This value was about 4-times larger than that reported recently.[16] We previously reported[4] that the quantity of hydroquinone-2-thiol adsorbed on the gold electrode was estimated to be 5.2×10^{-10} mol cm^{-2}, and, therefore, the occupied area of a hydroquinonethiol

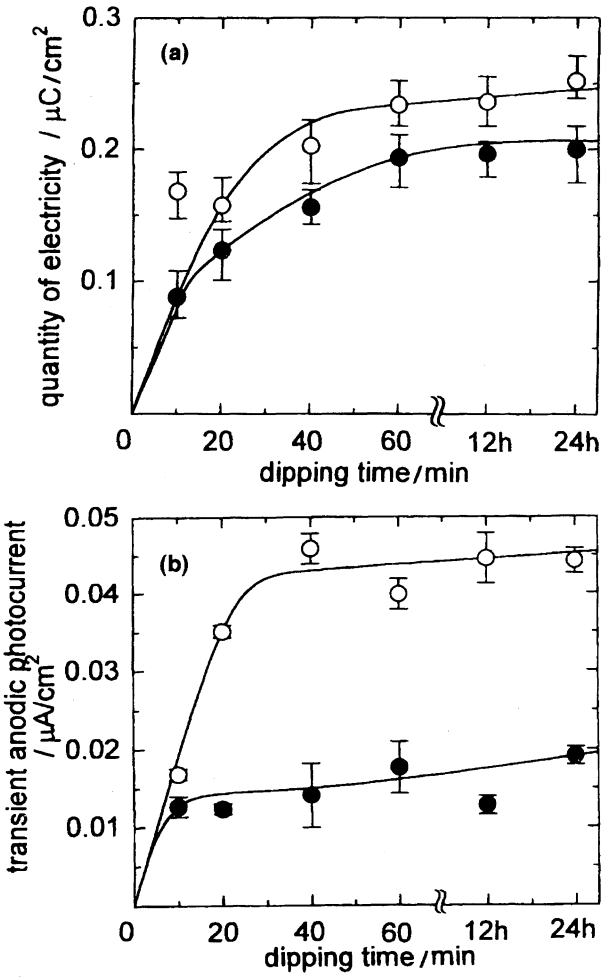

Fig. 3. Dependence of quantity of electricity for the anodic photoresponse (a) and transient photocurrent (b) on dipping time into reaction center suspension.
A hydroquinonethiol-modified gold electrode was dipped into native (●) or Q-depleted (○) RC suspension (A_{802} = 1). The other experimental conditions were the same as those in Fig. 2.

molecule was estimated to be 0.32 nm^2. These values agreed well with those obtained previously.[18] That is, the occupied area of a RC particle was equal to 48 nm^2, and a RC particle was immobilized on 150 molecules of adsorbed hydroquinone-2-thiol. This value was about 2-times larger than the calculated one for the closest packing of the particles. In addition, the quantity of electricity for anodic photoresponse by Q-depleted RC became about 1.2-times larger than that by native RC, as also shown in Fig. 3(a). This result suggests each of the following two reasons. First, the degree of orientation of Q-depleted RC particles becomes higher than that of native ones through an affinity of the hydroquinone-2-thiol molecule on the electrode to a vacant Q_B-site in RC particles. Second, the number of immobilized Q-depleted RC particles increases due to an enhancement of affinity between the RC particles and the hydroquinone-2-thiol molecule.

As mentioned above, the transient anodic photocurrent by Q-depleted RC was followed by rapid relaxation (Fig. 2d), whereas that by native RC was relaxed more slowly (Fig. 2c). In addition, a single RC particle can transfer just one electron to the electrode in response to illumination.[17] It thus seems probable that the generation of a pulse-like photocurrent is due to rapid electron transfer from the oriented immobilizing RC particles to the electrode, whereas the slow decay of photocurrent observed by native RC is due to electron transfer after a conformation change, such as a rotation of the particles on the electrode. Since we have estimated the quantity of electricity from the area bounded by the increase in the current in response to the illumination and a line tangent to the relaxation curve (insert in Fig. 2), the quantity of electricity for the photoresponse accompanying slow relaxation, as observed by native RC, involves that due to slow electron transfer from physically adsorbed particles. Thus, in order to accurately estimate the degree of orientation of RC particles, it becomes necessary to compare the transient photocurrent by Q-depleted RC with that by native RC. Figure 3(b) shows the dependence of the transient anodic photocurrent, instead of the quantity of electricity, on the dipping time. The transient photocurrent by Q-depleted RC increased with increasing time of dipping up to about 40 min, whereas those by native RC increased only during the first period of the dipping time, and was held approximately constant. In addition, the transient anodic photocurrent by Q-depleted RC became about 2.2-times larger than that by native RC. In other words, these results indicate that the difference in the quantity of electricity between the Q-depleted and native RC-immobilized electrodes is due to an increase in the number of immobilized RC particles, which enables rapid electron transfer from RC particles to the electrode, even during the first stage of the immobilization of RC particles. That is, the results suggest an increase in the degree of orientation of Q-depleted RC particles, rather than an increase in the number of immobilized Q-depleted RC particles.

If electrons ejected from the reaction center bacteriochlorophyll dimer (so-called Special Pair or P870) equilibrate with the electrode during the primary photochemistry, the photocurrent action spectrum should correspond to the absorption spectrum of the reaction centers. A photocurrent action spectrum was measured under a very weak light intensity (1—10 $J\,m^{-2}\,s^{-1}$); it coincided fairly well with the absorption spectrum of a RC suspension, revealing maxima at 600 (small), 800 (largest), and at 850 nm (large) (Fig. 4). These results indicate, as expected, that electron flow, upon illumination, takes place from P870 to the adsorbed *p*-benzoquinonethiol via the bacteriochlorophyll monomer, bacteriopheophytin, and ubiquinone A[19] to generate a transient anodic photocurrent.

Figure 5(a) shows dependence of transient photocurrent on applied potential. The photocurrent was observed in region more anodic than +200 mV up to +450 mV. The magnitude of photocurrent increased with increase in anodic potential up to +300 mV, and then decreased. Figure 5(b) shows electron flow in the reaction center particle, as mentioned above. The redox potential of P870 is determined to be +450 mV,[20] the result that transient photocurrent could not

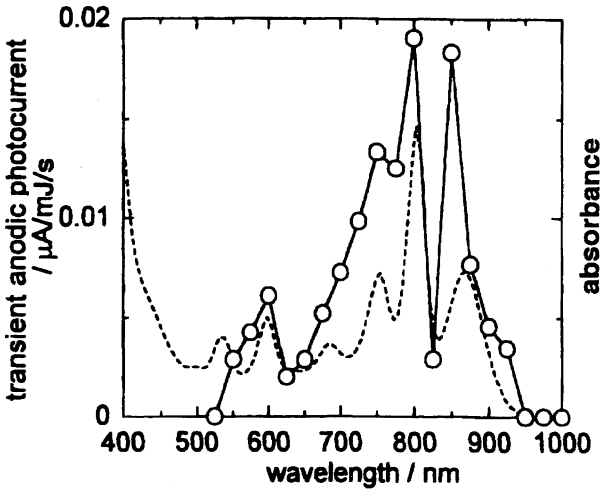

Fig. 4. Transient anodic photocurrent action spectrum by the Q-depleted RC immobilized on the hydroquinonethiol-modified gold electrode.
The dotted line shows the absorption spectrum of the Q-depleted RC suspension. The experimental conditions were the same as those in Fig. 2, except that the monochromatic light was illuminated at a low light intensity. The similar action spectrum was obtained using a native RC, although the values of photocurrent were somewhat smaller.

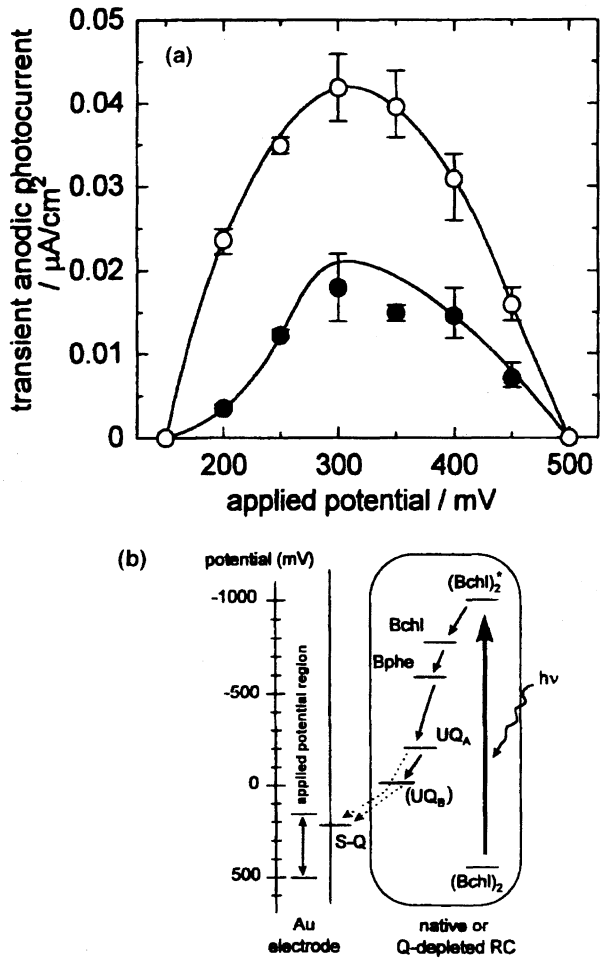

Fig. 5. Dependence of transient photocurrent on applied potential (a), and schematic representation for relationship of the redox potentials of electron transfer components in the reaction centers to the applied potential (b).
Symbols, ● and ○, represent the values of photocurrent by native and Q-depleted RC's, respectively. The experimental conditions were the same as those in Fig. 2, except that the applied potential was varied. Abbreviations in the Fig. (b) are as follows: $(BChl)_2$, reaction center bacteriochlorophyll dimer (P870); BChl, bacteriochlorophyll monomer; Bphe, bacteriopheophytin; UQ_A, ubiquinone A; UQ_B, ubiquinone B if present; S-Q, hydroquinone-2-thiol.

be observed in a region more anodic than +500 mV is due to the direct electrolytic oxidation of P870. In addition, the redox potential of hydroquinone-2-thiol adsorbed on the electrode was +220 mV at pH 7.5. This is thus the reason that a transient photocurrent could not be generated in a region more cathodic than +150 mV, in which the adsorbed hydroquinone-2-thiol was almost reduced and could not accept additional electrons from the reaction center particles.

The transient photocurrent also depended on the solution pH, showing a maximum around neutral pH (Fig. 6(a)). It has been reported[21] that the electron-transfer rate from ubiquinone A to B (k_{AB}) in reaction centers from *Rhodobacter sphaeroides* was essentially pH independent in the range between pH 5 and 8, and decreased above about pH 8, being attributed to the deprotonation of Glu-L212. Thus, the decrease in the transient photocurrent in the basic region may be attributed to the same phenomenon. On the other hand, the decrease in the acidic region seems to be explained from the view of the redox potential of adsorbed hydroquinone-2-thiol. The redox potential of adsorbed hydroquinone-2-thiol increased linearly with lowering the pH with a slope of −59 mV/pH (data not shown). Since the photocurrent was measured at +300 mV of the applied potential, quinonethiol was reduced almost completely below pH 5, and the electron transfer from ubiquinone A (or ubiquinone B if present) to the electrode (k_{AE} or k_{BE}) was interrupted (Figure 6(b)). This is the reason that the transient photocurrent could not be generated below about pH 5.

In addition, the transient photocurrent by Q-depleted RC depended on the illuminance, increasing with an increase in the illuminance up to about 6000 lx. and reaching a plateau, whereas that by native RC increased only in the low light intensity region and was held approximately constant up to 10000 lx. (Fig. 7(b)); also, the quantity of electricity by both RCs increased with increasing illuminance up to about 6000 lx., as shown in Fig. 7(a). That is, the quantity of immobilized RCs seems to be almost the same. In other words, the independency of the transient photocurrent by native RC upon illuminance seems to be due to photosaturation because of a small amount of immobilized RC particles enables rapid electron transfer. On the other hand, the result that the photosaturation could not be observed at the Q-depleted RC-immobilized electrode until reaching a strong illuminance region suggests an increase of the rapid electron transfer components. Thus, these results again suggest an increase in the degree of orientation of a Q-depleted RC particle.

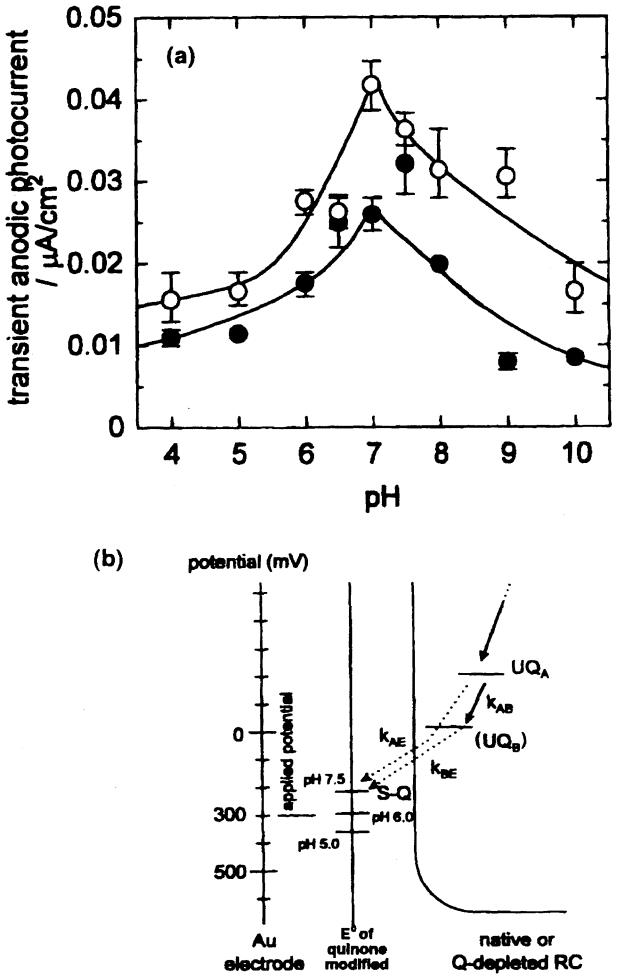

Fig. 6. Dependence of transient photocurrent on solution pH (a), and schematic representation for relationship of the redox potentials of electron transfer components in the reaction centers to that of hydroqiunone-2-thiol under the various pH (b).
Symbols, ● and ○, abbreviations, and the experimental conditions were the same as those in Fig. 5, except that the solution pH was varied and the applied potential was adjusted to +300 mV.

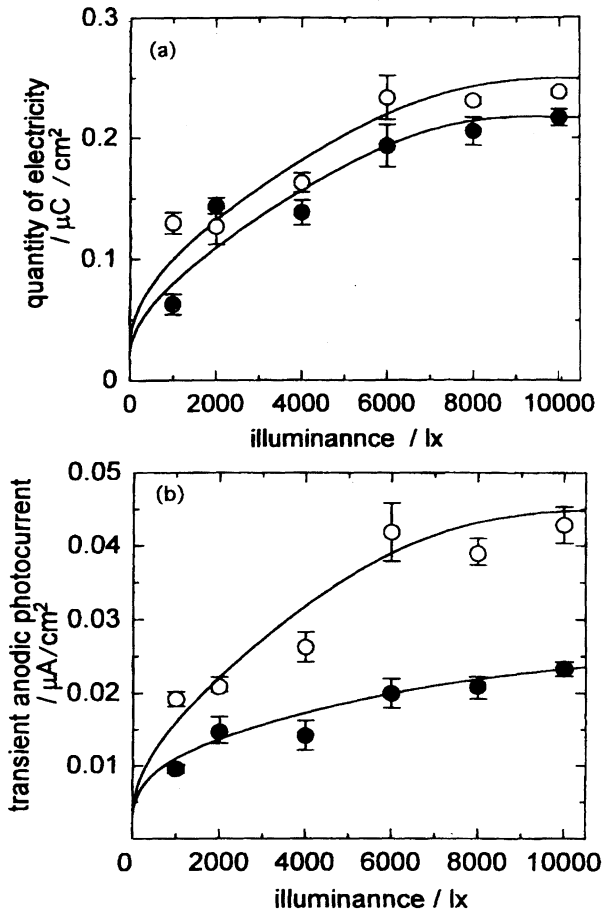

Fig. 7. Dependence of quantity of electricity for the anodic photoresponse (a) and transient photocurrent (b) on illuminance.
Symbols, ● and ○, represent the values of photoresponse by native and Q-depleted RCs, respectively. The experimental conditions were the same as those in Fig. 2, except that the illuminance was varied.

Table 1. Estimation of Transient Anodic Photocurrent and Quantity of Electricity by Reaction Center Complexes Immobilized on Hydroquinonethiol-Modified Gold Electrode

RC	Transient anodic photocurrent / nA cm^{-2}	Quantity of electricity / μC cm^{-2}
Native	18	0.193
Native*1	19	0.192
Native*2	16	0.199
Q-depleted	39	0.233
Q-depleted*1	54	0.343
Q-depleted*2	15	0.104

A hydroquinonethiol-modified electrode was pre-electrolyzed in a Tris buffer (pH 7.5) at either +400*1 or +50*2 mV before immobilizing RCs in order to oxidize or reduce completely the modified quinonethiol.

Furthermore, the quantity of electricity for the photoresponse by Q-depleted RC became about 50% larger upon pre-electrolyzing at +400 mV before immobilizing the reaction center particles than in the case of using an untreated hydroquinonethiol-modified electrode, and decreased to about 45% upon pre-electrolyzing at +50 mV, as shown in Table 1. Such a tendency could not be observed using native-RC, as also shown in Table 1. It has been reported[22] that the oxidized form of ubiquinone B is bound more tightly to the Q_B-site in the RC particle through hydrogen-bond formation than in its reduced form. These results again indicate that the vacant Q_B-site plays some roles in enhancing the photocurrent. That is, the degree of orientation of Q-depleted RC particles becomes higher through a binding affinity between the Q_B-site in the reaction center particles and the *p*-benzoquinonethiol molecules modified on the gold electrode. If so, it is expected that the reaction center particles can be immobilized more tightly by using a quinonyl compound having a relatively long mercaptoalkyl side chain, because the Q_B-site is present at the interior side of the reaction center particle,

Table 2. Estimation of Transient Anodic Photocurrent and Quantity of Electricity by Q-Depleted RCs in the Absence or Presence of an Electron Donor

Electron donor	Transient anodic photocurrent	Quantity of electricity
	nA cm^{-2}	$\mu C\ cm^{-2}$
None	36	0.235
Cytochrome c_2 (200 μM)	35	598.2

as schematically shown in Fig. 1(b). We have attempted to modify a gold electrode with 2-(2′-mercaptoethylamino)-*p*-benzoquinone, and then the immobilization of Q-depleted RC particles on the modified electrode. However, a photocurrent by Q-depleted RC was hardly observed, and the reason for this did not become completely clear.

It is well known[23] that the intrinsic electron donor to native RC is a reduced form of cytochrome c_2, and that the native RC can successively perform a photochemical electron-transfer reaction through the reduction of photo-oxidized bacteriochlorophyll with the reduced form of cytochrome c_2. In addition, we have already reported[24] that cytochrome c_2 could not show any rapid electron transfer at normal metal electrodes. Thus, a large excess (200 μM) of reduced cytochrome c_2 was added into the electrolytic solution. Then, a continuous flow of the anodic photocurrent was observed over a period of 5 h with the same magnitude as the transient photocurrent, as also shown in curve **e** of Fig. 2. The value of the anodic photocurrent and the quantity of electricity for the anodic photoresponse are summarized in Table 2. These results indicate that the immobilized reaction centers can transfer electrons over 2500 cycles of the turnover number.

In conclusion, the largest anodic photoresponse by immobilized reaction centers could be observed using Q-depleted RC and with the pre-oxidation of adsorbed hydroquinone-2-thiol, indicating that the degree of orientation of the reaction center particles increases through a binding affinity between the vacant Q_B-sites of the particles and *p*-benzoquinonethiol modified on a gold electrode surface. However, the reason for this is not completely clear. This anodic photoresponse could be elongated for over 5 h (2500 cycles of turnover number) by adding cytochrome c_2 into the electrolytic solution.

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