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Effects of the incorporation of silver and gold nanoparticles on the photoanodic properties of rose bengal sensitized TiO_2 film electrodes prepared by sol–gel method

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Abstract

Rose bengal-deposited TiO_2 film electrodes bearing dispersed Ag or Au nanoparticles were prepared by the sol–gel method. The dye-induced visible region photoresponse of the electrodes decreased with increasing Ag content up to a mole ratio of $Ag/TiO_2 = 0.0207$, while the UV photoresponse increased. On the other hand, the dye-induced visible region photoresponse decreased to a less extent by incorporation of a larger amount of Au particles of $Au/TiO_2 = 0.06$, along with decreased UV photoresponse. The effects of the metal particles on the dye sensitization of the electrodes were discussed in terms of band edge fluctuation induced by the surface metal particles, Schottky barriers at TiO_2/metal interfaces, and surface plasma resonance.

Keywords: TiO_2 electrode; Photoanode; Surface plasma resonance; Metal particle; Dye-sensitization; Sol-gel method

1. Introduction

Local enhancement of oscillating electromagnetic fields by the surface plasma resonance of fine metal particles is attracting much attention, because it can enhance

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fluorescence of dyes [1–3], third-order nonlinear optical process [4] and Raman scattering from molecules (SERS) [5]. Besides the optical processes mentioned above, Nitzan and Brus [6] pointed out for the first time the possibility of enhancement of photochemical processes by surface plasma resonance, based on a theoretical discussion. Later, Chen and Osgood [7] experimentally demonstrated that photodissociation of dimethyl cadmium can be enhanced by surface plasma resonance of cadmium metal particles.

Dye sensitization is one of the methods to extend the photoresponse of wide gap semiconductor electrodes like TiO_2 to the visible region [8, 9]. In practice, the sensitizing quantum yield per absorbed photon tends to be quite low, however, which is thought to be due to a fast back-reaction of the injected electrons from the semiconductor conduction band to the oxidized dye molecules as discussed by Spitler [10]. In order to overcome this problem, O'Regan and Grätzel [11] prepared dye-sensitized, high surface area anatase electrodes, which exhibited high yields for the collection of photoexcited electrons from the adsorbed dyes because of their large surface area. Another possible idea for enhancing the sensitizing efficiency is to utilize the enhancement of the photochemical process of the sensitizers by surface plasma resonance of small metal particles. Incorporation of small metal particles in dye-sensitized semiconductor electrodes is expected to enhance the electronic excitation of the dyes and consequently the injection of electrons into the electrode conduction band.

Recently, we have prepared TiO_2 film electrodes containing Ag or Au metal particles by the sol–gel method, and found that the visible region photoresponse emerged when the metal particles were embedded [12]. We attributed this phenomenon to the enhancement of the photoexcitation of the surface state electrons by surface plasma resonance. Furthermore, we have studied the effect of Au particle incorporation on the photoanodic properties of TiO_2 film electrodes with a variety of deposited dyes [13]. Unfortunately, we found that the sensitized visible region photoresponse was decreased when Au particles were incorporated, which was ascribed to the retardation of electron conduction caused by Schottky barriers forming at TiO_2/Au interfaces. The extent of the photoresponse reduction, however, was smaller when the surface plasma resonance and the optical absorption of dyes well overlapped each other in wavelength, suggesting the possible enhancement of the photochemical process of the sensitizers.

In the present work, we study effects of metal particles on dye sensitization of TiO_2 film electrodes. Ag and Au were employed as the metal particles to be embedded and rose bengal as the sensitizing dye. Sol–gel method was used for sample preparation.

2. Experimental

2.1. Sample preparation

Film electrode samples were prepared on SnO_2-coated SiO_2 glass (nesa silica glass) substrates by the sol–gel method. The electrode samples were prepared so that they are composed of an undoped TiO_2 base layer and a TiO_2 overlayer with or without embedded Ag or Au particles. Table 1 shows the molar compositions of the starting solutions. Solution BS in Table 1 was served as a coating solution for the base layer, and solutions AU0 – AU06 and AG0 – AG02 in Table 1 were served for the overlayer. The mole ratios $Ag/TiO_2 = 0.0062$ and 0.0207 correspond to the volume fraction of Ag particles of 0.3% and 1% in the Ag–TiO_2 composite overlayers, respectively, when the composites are assumed to be totally free of pores. On the same assumption the mole ratio $Au/TiO_2 = 0.06$ corresponds to the volume fraction of Au particles of 3% in the Au–TiO_2 composite layer. For preparing solution BS, a solution of deionized water, nitric acid (Nacalai Tesquie, Inc., 60%) and a half of the prescribed amount of ethanol (Nacalai Tesque, Inc., 99.5%) was added dropwise to titanium tetraisopropoxide (Wako Pure Chemical Industries, Ltd., 95%) diluted with the rest of ethanol. For preparing solutions AG0–AG02, a solution of deionized water and a half of the prescribed amount of isopropanol (Nacalai Tesque, Inc., 99.5%) with or without silver nitrate (Wako Pure Chemical Industries, Ltd., 99.8%) was added dropwise to a mixture of titanium tetraisopropoxide, diethanolamine (Wako Pure Chemical Industries, Ltd., 99%) and the rest of isopropanol. For preparing solutions AU0–AU06, a solution of deionized water, hydrochloric acid (Wako Pure Chemical Industries, Ltd., 36%) and a half of the prescribed amount of ethanol with or without chloroauric acid tetrahydrate (Nacalai Tesque, Inc., 99%) was added dropwise to a mixture of titanium tetraisopropoxide, acetic acid (Nacalai Tesque, Inc., 99.7%) and the rest of ethanol. Mixing was always performed at 0°C under vigorous stirring.

A nesa silica glass substrate was dipped into solution BS immediately after preparation and withdrawn at a constant rate of 1 cm min^{-1} and heated at 500°C for 10 min. The dip-coating and heat-treatment were repeated 8 times to obtain the base layer. Then overlayers were deposited on the base films using solutions AG0–AG02 and AU0–AU06. The dip-coating and heat-treatment at 500°C for 10 min were repeated twice, followed by the final heat-treatment at 600°C for 10 min. All the film samples were anatase, which was confirmed by X-ray diffraction measurement. Precipitation of nanometer sized metal particles was confirmed by TEM observation [12]. Hereafter, the electrode samples prepared from solutions AG0 – AG02 and AU0 – AU06 in Table 1 will be called AG series and AU series samples, respectively.

Deposition of the dye was carried out by immersing the TiO_2 electrode samples in a 10^{-4} M ethanol solution of rose bengal (Nacalai Tesque, Inc., > 85%) at room temperature for 24 h and then drying them at 200°C for 10 min.

2.2. Measurements

Optical absorption spectra of the film electrode samples were measured by a Hitachi U-3500 spectrophotometer using a nesa silica glass substrate as the reference sample.

The current-potential curves were measured in a cell consisting of the electrode sample as the working electrode, SCE as the reference electrode, platinized Pt as the counter electrode and a buffer solution of pH 7 as the supporting electrolyte. The buffer solution was an aqueous solution of 0.2 M $Na_2B_2O_7$, 0.14 M H_2SO_4 and 0.3 M Na_2SO_4. The potential of the working electrode was controlled with a Hokuto Denko

Table 1

Compositions of the starting solutions

Solution	Mole ratio									
	$Ti(OC_3H^i_7)_4$	Au[a]	Ag[b]	H_2O	C_2H_5OH	i-C_3H_7OH	HNO_3	HCl	CH_3COOH	$NH(CH_2CH_2OH)_2$
Base layerBS	1			1	10		0.2			
Overlayer										
AG0	1			2		18				1
AG006	1		0.0062	2		18				1
AG02	1		0.0207	2		18				1
AU0	1			1	8			0.27	1	
AU06	1	0.06		1	8			0.27	1	

[a] Added as $HAuCl_4.4H_2O$.

[b] Added as $AgNO_3$.

HA-501M potentiostat. An Ushio Denki 500 W xenon lamp was used for illuminating the electrode sample. Action spectra were measured at a bias potential of 1 V vs. SCE using xenon lamp light monochromatized with a Shimadzu SPG-100ST monochromator. The intensity of the monochromatized light was measured with an Advantest TQ8210 optical powermeter.

3. Results

3.1. Optical absorption spectra

As was previously studied [12], X-ray diffraction measurement showed that the electrode samples were crystallized in the form of anatase, and transmission electron microscopic observation revealed precipitation of metallic particles of 6 – 20 nm in size in the anatase matrices. Fig. 1a and Fig. 1b show the optical absorption spectra of

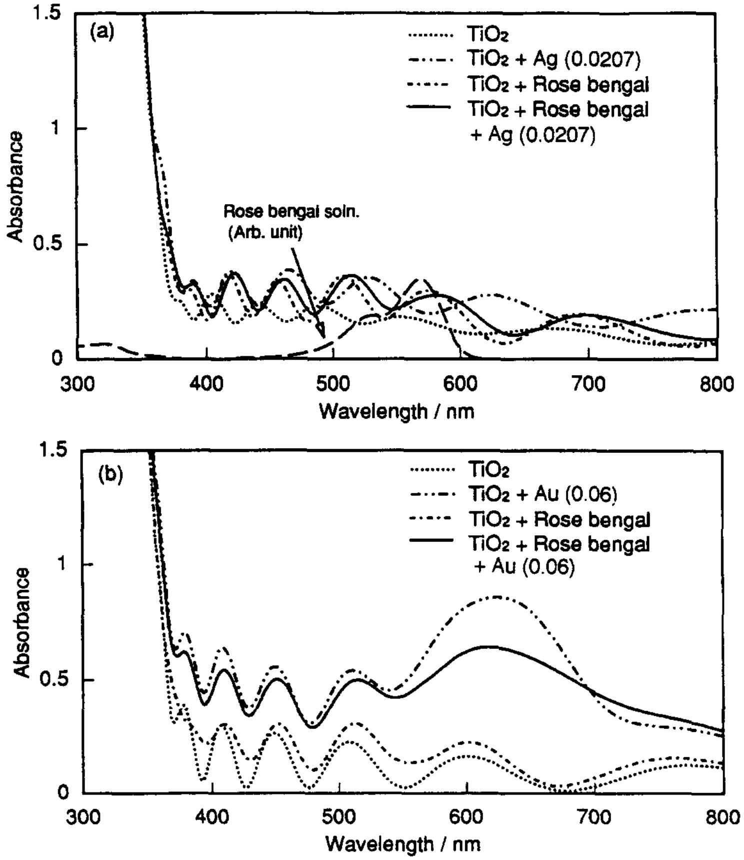

Fig. 1. Optical absorption spectra of (a) AG and (b) AU series film electrodes with or without deposited rose bengal and embedded metal particles.

AG and AU series electrode samples, respectively. The absorption spectrum of the rose bengal solution is also shown in Fig. 1(a), which was measured by using a dye solution of 10^{-4} M sandwiched by two slide glass substrates. Ripples observed in the spectra are due to the interference of light. In AG series samples, the absorption due to surface plasma resonance was small and broad, probably because of a small amount and large size distribution of the Ag metal particles. In contrast, an evident peak due to Au metal particles was observed around 620 nm as seen in Fig. 1(b), which is thought to result from a larger amount of the particles. It should be noted that in AU series samples the deposition of rose bengal decreased the absorption around 620 nm and slightly increased the absorption at 700 – 800 nm. The amount of the absorbed dye per electrode surface area was calculated to be 1.1×10^{-9} mol cm^{-2}.

3.2. Photoelectrochemical properties

Fig. 2a and Fig. 2b show the current–potential curves of dye-deposited AG and AU series electrode samples, respectively, in the dark and under illumination by xenon lamp white light. The anodic photocurrent of the rose bengal-deposited AG series electrode samples increased when Ag/TiO_2 mole ratio increased to 0.0207 as seen in Fig. 2(a). On the other hand, incorporation of Au metal particles (Au/TiO_2 = 0.06) decreased the anodic photocurrent of the dye-deposited sample at bias potentials positive of 0.8 V vs. SCE (Fig. 2(b)).

Steep increase in dark- and photocurrent was observed for AG series samples at bias potentials positive of 1.3 and 1.8 V vs. SCE, respectively (Fig. 2). On the other hand, such an increase in current at these positive bias potentials was not observed in AU series samples. The onset of the dark current of the electrode samples at these positive bias potentials are of course due to the tunneling effect through the depletion layer of the TiO_2 electrodes. As discussed in a previous paper [12], the increased current at highly positive potentials with increasing amount of Ag particles can be assigned to the increased evolution of O_2 gas catalyzed by the Ag metal particles; the more negative oxygen evolution potential at Ag metal may cause the more negative onset potential for the anodic dark current and the larger apparent anodic photocurrents at the positive bias potentials for the Ag dispersed electrodes than the Au dispersed electrodes.

Fig. 3a and Fig. 3b show the action spectra of dye-deposited AG and AU series electrode samples, respectively, measured at a bias potential of 1 V vs. SCE. Here, currents are divided by the intensity of the incident light at each wavelength and the illuminated area. Anodic photoresponse was observed in the visible region peaking at 560 nm, which agrees with the maximum optical absorption wavelength of the rose bengal solution. As seen in Fig. 3(a) the visible region photoresponse decreased significantly with increasing Ag particle content from Ag/TiO_2 = 0.0062 to 0.0207. The incorporation of Au metal particles of Au/TiO_2 = 0.06 also decreased the photoresponse at 450–600 nm (Fig. 3(b)), but the extent of the decrease was much smaller than in AG series samples. It should be noted that the Au particle incorporation increased the photoresponse at longer wavelengths of 600–800 nm. UV photoresponse slightly

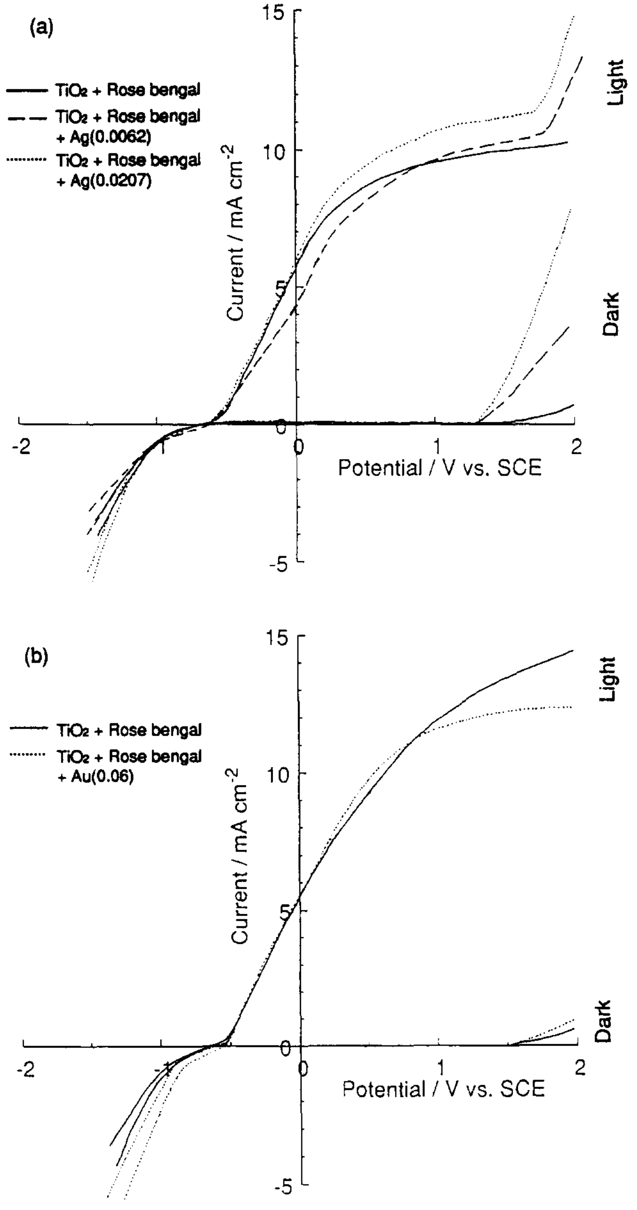

Fig. 2. Current–potential curves of rose bengal-deposited (a) AG and (b) AU series film electrodes with or without embedded metal particles.

increased when Ag particles of Ag/TiO_2 = 0.0207 were incorporated, while it decreased when Au particles were incorporated. The increase and decrease in the anodic currents by Ag and Au particle incorporation as seen in Fig. 2 are ascribed to these increase and decrease in the UV photoresponse, respectively.

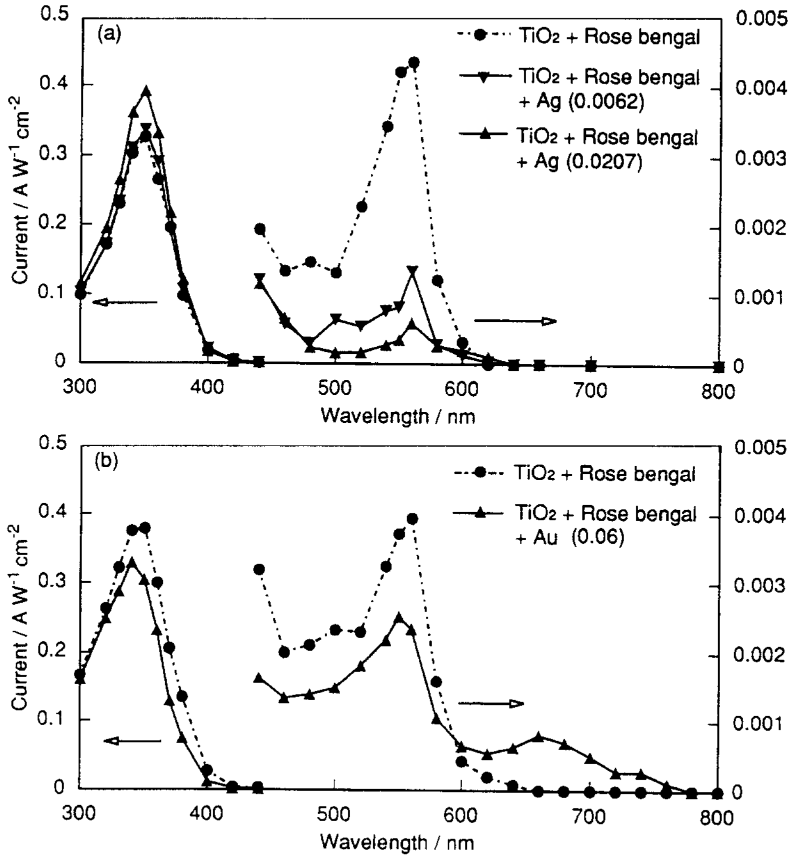

Fig. 3. Action spectra of rose bengal-deposited (a) AG and (b) AU series film electrodes with or without embedded metal particles.

4. Discussion

4.1. Band model illustration

Band models can be illustrated for the present electrode samples by taking account of the Schottky barriers formed at the TiO_2/metal and TiO_2/solution interfaces as in the same manner as described elsewhere [12]. Fig. 4 shows the band models of the present electrode samples under illumination in an aqueous solution of $pH = 7$ at a bias potential of 1 V vs. SCE. Curves 1 and 2 correspond to the band arriving at the bare and metal covered parts of the TiO_2 surface, respectively. The bare TiO_2 surface has the conduction band edge at -0.5 V vs. SCE, which corresponds to the flat band potential of the present electrodes. The conduction band drops by 1.5 V in the interior of the electrode because of the anodic polarization with a bias potential of 1 V vs.

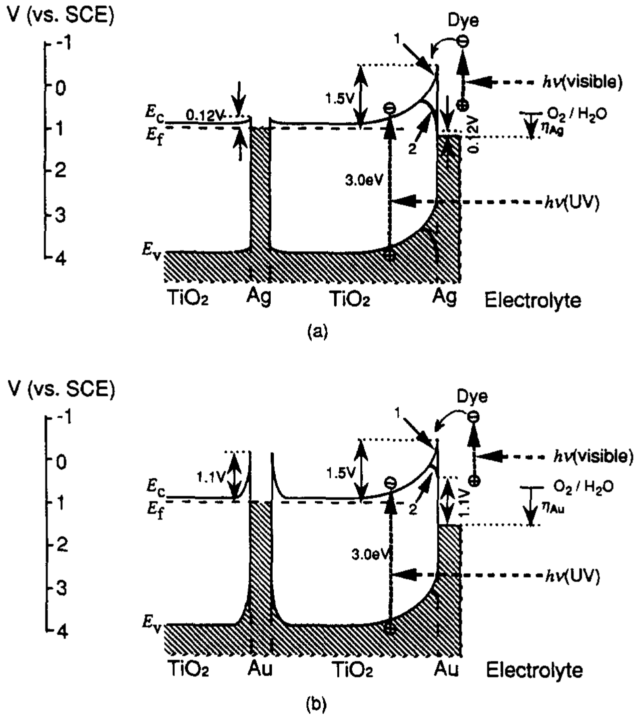

Fig. 4. Energy band models for TiO_2 film electrodes with deposited rose bengal molecules and (a) Ag and (b) Au particles at a bias potential of 1 V vs. SCE in an electrolyte solution of pH = 7. Curves 1 and 2 correspond to the band arriving at the bare and metal covered parts of the TiO_2 surface, respectively. η_{Ag} and η_{Au} denote the overvoltage of Ag and Au for O_2 gas generation, respectively.

SCE. Since the work function of silver, ϕ_{Ag} and gold, ϕ_{Au}, are 4.12 and 5.1 eV, respectively, and the electron affinity of TiO_2 is 4.0 eV, a Schottky barrier of 0.12 V height is formed at the TiO_2/Ag interface and that of 1.1 V height at the TiO_2/Au interface. According to Nakato et al. [14, 15], who have postulated the band fluctuation of TiO_2 electrodes with Au particles deposited on the surface, the conduction band edge of TiO_2 at the TiO_2/metal interface should be dropped as shown by curves 2 in Fig. 4 because of the barrier heights of 0.12 and 1.1 V for the TiO_2/Ag and TiO_2/Au interfaces, respectively, which are smaller than 1.5 V at the plain TiO_2/electrolyte interface. In addition, the Fermi energy of the surface metal particles lowers under illumination as experimentally demonstrated by Nakato et al. [16, 17]. The redox potential of O_2/H_2O is 0.57 V vs. SCE, and the oxygen overpotentials of Ag and Au metal electrodes are 0.6 and 0.96 V, respectively, at a current density of 10 mA cm^{-2} [18]. Therefore, the oxygen evolution potentials at Ag and Au metal electrodes are calculated to be about 1.2 and 1.5 V vs. SCE, respectively.

4.2. Effects of metal particles on the electrode characteristics

Based on a band model similar to that illustrated above, several effects of metal particles on the anodic properties of TiO_2 electrodes were discussed in a previous paper [12]. The following mechanisms would increase the photocurrent:

(1) The surface metal particles and the metal particle-induced surface states can electrocatalytically promote the transportation of UV light-generated holes from the valence band to the electrolyte solution.

(2) The surface plasma resonance of the metal particles enhances the visible light excitation of electrons.

On the other hand, the following mechanisms would decrease the photocurrent:

(3) Schottky barriers at the TiO_2/metal interfaces in the interior reduce the mobility of the electrons and holes in the conduction and valence bands, respectively.

(4) The surface metal particles and the metal particle-induced surface states act as recombination centers of the UV light-generated electron/hole pairs.

(5) The fluctuation of the conduction band edge caused by the surface metal particles retards the transfer of the conduction band electrons from the surface to the interior.

When the optical absorption wavelength of the dye overlaps the surface plasma resonance of the metal particles, the electronic excitation of the dye will be enhanced by the large oscillating electric field resulting from the surface plasma resonance [1, 6, 19, 20], which is expected to cause enhanced dye sensitization. The dye-induced photoresponse in the visible region was decreased, however, when Au or Ag metal particles were incorporated in the present dye-deposited TiO_2 electrodes. As discussed in a separate paper [13], one reason for the decreased dye sensitization is the retarded transportation of the conduction band electrons caused by the Schottky barriers at TiO_2/metal interfaces; the barrier can disturb the electron transport and also may trap the electrons in the depletion layer around metal particles. Another possible reason is the back-reaction of the electrons from the conduction band to the dyes, which is promoted by the metal particle-induced band edge fluctuation; the lowered edge of the conduction band (curve 2 in Fig. 4) can retard the electron transport from the conduction band edge to the interior.

It should be noticed that the incorporation of Ag particles did not affect or rather increased the UV photoresponse although it decreased the visible region photoresponse (Fig. 3(a)). As discussed in a separate paper [13], the increase in the UV photoresponse of the Ag-doped electrode is due to the electrocatalytic effect of the surface Ag particles (effect (1) mentioned above), which dominates over the recombination effect (effect (4)) and the fluctuated band edge effects (effect (5)). This indicates that the reduction of the visible region photoresponse by Ag particle incorporation is not caused by the Schottky barriers at TiO_2/Ag interfaces, which should also decrease the UV response via disturbed transportation of the conduction band electrons. Therefore, it can be concluded that the reduction of the visible region photoresponse by Ag particle incorporation results from the band edge fluctuation rather than from the Schottky barriers. The smaller drop of the band edge in the Au-doped electrode can be thought to be the cause of the smaller reduction in the visible region photoresponse than the Ag-doped electrode. Decrease in the UV photoresponse in the Au-doped electrode is due to the higher Schottky barriers at TiO_2/Au interfaces.

Another more important factor that gave rise to the smaller reduction in the visible region in the present Au-doped electrode is the larger surface plasma resonance and the overlap of the surface plasma resonance and optical absorption of rose bengal. The decrease in the absorbance at 600 nm and the slight increase at longer wavelengths were observed when the Au particles were incorporated in the rose bengal-deposited electrode sample (Fig. 1(b)). This implies the strong coupling between the rose bengal molecules and the Au particles [1, 21, 22]. This strong coupling effectively enhances the photoexcitation of the electrons in the dye molecules, leading to the smaller reduction in the visible region photoresponse. On the other hand, since the surface plasma resonance in the present Ag-doped electrodes was small and broad, the photoexcitation of electrons in the dye molecules was not enhanced efficiently.

The effect of the present metal particles on the photoanodic properties of the rose bengal-deposited TiO_2 electrodes can be summarized as follows: The Ag particles

(a) showed smaller and broad surface plasma resonance, leading to less efficient enhancement of photoexcitation of electrons in the dye molecules, and

(b) induced large drop of the TiO_2 band edge, promoting the back-reaction of the electrons from the conduction band to the dye molecules; both (a) and (b) effectively reduced the visible region photoresponse, and

(c) formed low Schottky barriers in the interior, not giving rise to the reduction of UV photoresponse.

The Au particles

(a′) showed large surface plasma resonance, leading to efficient enhancement of photoexcitation of electrons in the dye molecules, and

(b′) induced small drop of the TiO_2 band edge, not efficiently promoting the back-reaction of the electrons from the conduction band to the dye molecules; both (a′) and (b′) suppressed the reduction of the visible region photoresponse, and

(c′) formed high Schottky barriers in the interior, giving rise to the reduction of the UV photoresponse.

Dissipative energy transfer from the excited dye molecules to the metal particles is another factor that decreased the dye sensitization. It is the dipole–dipole coupling between the dye molecules and the large, induced dipoles in the metal particles which enhance the optical absorption of dyes. Energy can also be transferred dissipatively; however, from the excited dye molecules to higher multipole resonance modes as suggested theoretically by Nitzan and Brus [6] and experimentally by Wokaun et al. [20]. Because the local field enhancement and the loss of excitation energy by energy transfer have different dependence on the dye-metal separation [6, 20], photochemical processes are suppressed for dye molecules adsorbed directly on the metal particles, but increase to a maximum at a well defined dye–metal separation. There may be many dye molecules that are directly adsorbed on the metal particles in the present electrode samples, resulting in the increased dissipative energy transfer from the dyes to the metal particles.

Based on the discussions made in the present and separate [13] papers, desired conditions for enhanced sensitization is considered below.

(i) Metals and dyes should be selected, of course, so that their optical absorption well overlaps.

(ii) Metal particles should be placed only on the electrode surface, but not in the interior, in order to avoid retardation of electron conduction in the interior.

(iii) Bias potential and metal should be selected so that bias potential E_b, flat band potential E_{fb} and electron affinity χ_s of TiO_2, and work function of metal ϕ_m have the following relation;

$$E_b - E_{fb} \leqslant \phi_m - \chi_s .$$

This avoids the lowering of the semiconductor band edge at the part covered with metal, allowing the electron transfer from the band edge to the interior.

(iv) Definite separation in nanometer scale between dye molecules and metal particles should be attained, in order to avoid the dissipative energy transfer from excited dye molecules to metal particles.

5. Conclusions

Rose bengal-deposited TiO_2 film electrodes containing dispersed Ag or Au nanoparticles were prepared by sol–gel method. The dye-induced visible region photoresponse of the electrodes decreased with increasing Ag content up to a mole ratio of $Ag/TiO_2 = 0.0207$, while the UV photoresponse increased. The decrease in the visible photoresponse in the Ag-doped electrodes was thought to be due to the fluctuation of the TiO_2 conduction band edge caused by the Ag particles on the electrode surface and to the small and broad surface plasma resonance. On the other hand, the dye-induced visible region photoresponse decreased to a less extent by a larger amount of Au particles of $Au/TiO_2 = 0.06$, accompanied with the decrease in the UV photoresponse. The larger surface plasma resonance and a smaller band edge fluctuation was thought to suppress the decrease in the visible region photoresponse.

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