

# The Photocurrent of Dye-Sensitized Solar Cells Enhanced by the Surface Plasmon Resonance

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To evaluate the effect of the surface plasmon resonance of Ag nanoparticles on dye-sensitized solar cells, we measured the photocurrent of electrochemical cells using dense dye-adsorbed TiO<sub>2</sub> thin films with and without Ag nanoparticles at different adsorbed-dye concentrations. At lower dye concentrations, the photocurrent of the cells with Ag was found to be enhanced by the effect of the surface plasmon resonance compared to that of the cells without Ag. On the other hand, the photocurrent of the cells with Ag decreased at higher dye concentrations, which was caused by increased trap levels and band-edge fluctuations with Ag incorporation. It is revealed that the control of the structure and quantity of Ag particles is important to apply the surface plasmon resonance effect to dye-sensitized solar cells.

## Introduction

Dye-sensitized solar cells (O'Regan and Grätzel, 1991) have recently attracted much attention because of their comparably high conversion efficiency and low cost. However, it is still required to enhance the efficiency of the cells for application. The photocurrent of the dye-sensitized solar cells originates from the optical absorption of dyes adsorbed on TiO<sub>2</sub> electrodes. Therefore, the conversion efficiency depends on the optical absorption spectrum of dye that is the highest at the absorption peak of about 550 nm for a Ru-complex dye and decreases at longer wavelengths, which corresponds to the smaller absorption coefficient (Nazeeruddin *et al.*, 1993). In order to enhance the optical absorption of dyes at longer wavelength, we utilized the surface plasmon resonance of silver particles, which has been proved to enhance Raman scattering (Jeanmaire and Van Duyne, 1977; Albrecht and Creighton, 1977), optical absorption (Craighead and Glass, 1981; Eagan, 1981), and photoluminescence (Glass *et al.*, 1980; Ishikawa and Okubo, 2003) of dyes. In our previous paper (Ihara *et al.*, 1997), the optical absorption of Ru(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub> (Ru-dye) increased remarkably near Ag nanoparticles. In the continued work, we examined the photoresponse of photochemical cells using dense Ru-dye-adsorbed TiO<sub>2</sub> films as the anodes with and without evaporated Ag nanoparticles, and

clarified that the photocurrent originated from the carriers of Ru-dye was enhanced with Ag nanoparticles (Wen *et al.*, 2000). We also showed a decrease of the photocurrent in the visible region by increasing the mass-equivalent Ag film thickness.

In this paper, we examine the effects of the surface plasmon resonance of Ag on the photocurrent by changing the quantity of adsorbed dye in the same condition of Ag deposition.

## 1. Experimental

The electrochemical cell is prepared in the same manner as described previously (Wen *et al.*, 2000). The anode electrode is composed of a dense Ru-dye adsorbed TiO<sub>2</sub> thin film and transparent conducting-SnO<sub>2</sub> glass. The dense TiO<sub>2</sub> film is used as the anode, because structural changes of the porous TiO<sub>2</sub> induced by Ag nanoparticles can be eliminated to clarify the surface plasmon resonance effect of Ag, and Ag nanoparticles can be easily formed on the TiO<sub>2</sub> by thermal evaporation. The cathode is Pt-sputtered transparent conducting-SnO<sub>2</sub> glass. The electrochemical cell without Ag is prepared by sandwiching the redox solution containing Co(1,10-phenanthroline)<sub>3</sub><sup>2+</sup> (Co(phen)<sub>3</sub><sup>2+</sup>) and Co(1,10-phenanthroline)<sub>3</sub><sup>3+</sup> (Co(phen)<sub>3</sub><sup>3+</sup>) between both electrodes. After photoelectric measurements, the cell without Ag is decomposed and the electrodes are quickly rinsed with acetonitrile. Then, Ag nanoparticles are deposited by thermal evaporation on the dried anode. The cell with Ag was prepared with the redox solution, and measured the photoelectric properties. The schematic view of the cell is

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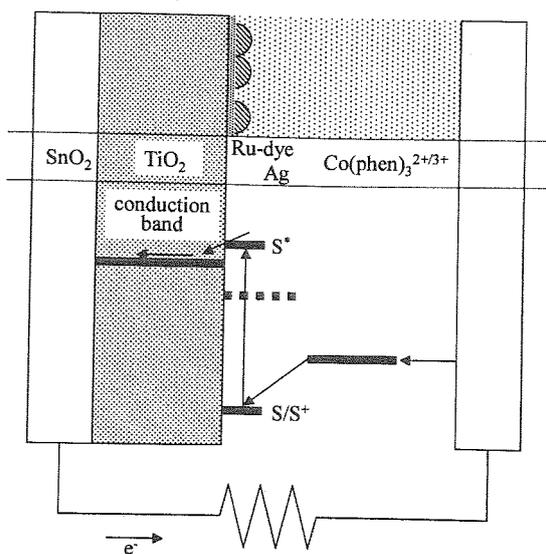


Fig. 1 Schematic view of a dye-sensitized cell with Ag nanoparticles

shown in Figure 1.

The  $\text{Co(phen)}_3^{2+}/\text{Co(phen)}_3^{3+}$  solution is prepared by dissolving  $0.3 \text{ mol/dm}^3$  of  $\text{Co(phen)}_3(\text{CF}_3\text{SO}_3)_2$  and  $0.04 \text{ mol/dm}^3$  of  $\text{Co(phen)}(\text{CF}_3\text{SO}_3)_3$  in a mixture of propylene carbonate and ethylene carbonate. The dense  $\text{TiO}_2$  films are deposited by laser ablation with a thickness of about 1  $\mu\text{m}$  on transparent, conducting- $\text{SnO}_2$ -glass films and annealed in the air at  $500^\circ\text{C}$  for three days. Dye-sensitized films are prepared by dipping the films into a Ru-dye solution after annealing. The photocurrent of the cells with and without Ag is measured under illumination of an AM1.5 light with a UV cut filter (under 400 nm). The action spectra of the cells with and without Ag are obtained under excitation by a monochromatic light. We also measure the action spectra of the cells with and without Ag using a monochromatic light with UV light excitation by a mercury lamp that has strong spectral lines at 365.0, 404.7 and 546.1 nm. The action spectra with UV light excitation is calculated from the photocurrent with a monochromatic light and UV light by subtracting the background photocurrent with the UV light.

In this study, the quantity of adsorbed Ru-dye is changed by altering the dipping time in its solution. The structure of Ag nanoparticles on dye-adsorbed  $\text{TiO}_2$  films is observed by FE-SEM at different concentrations of adsorbed dye.

## 2. Results

Figure 2 shows typical action spectra of photochemical cells using a dye-sensitized  $\text{TiO}_2$  film with and without Ag nanoparticles. Higher efficiency peaking at 380 nm is attributed to the photocurrent generated from  $\text{TiO}_2$ , because the peak can also be observed

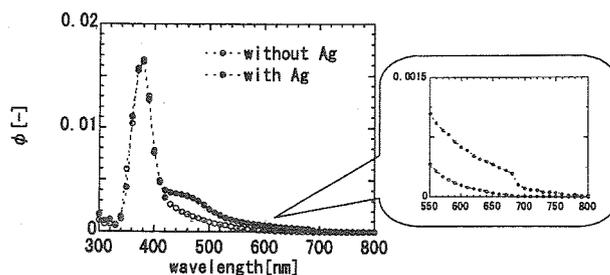


Fig. 2 Typical action spectra of a Ru-dye-sensitized cell with and without Ag nanoparticles

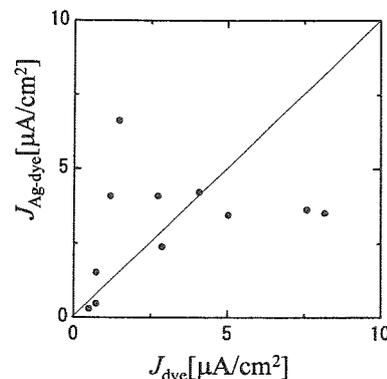


Fig. 3 Calculated photocurrent density of Ru-dye-sensitized cells with and without Ag using action spectra

for a cell composed of a  $\text{TiO}_2$  electrode without being dipped in a dye solution. The photocurrent due to the Ru-dye is observed in visible region and the incident photon-to-current conversion efficiency (IPCE) is in the order of 0.1%.

In Figure 3,  $J_{\text{Ag-dye}}$  and  $J_{\text{dye}}$  denote the photocurrent density of cells with and without Ag, respectively, calculated from the measured efficiency with Eq. (1) based on the solar spectrum of AM1.5 in the spectral range of 550–800 nm.

$$J = \int_{550}^{800} \frac{e}{hc} \lambda \cdot P(\lambda) \cdot \phi(\lambda) d\lambda \quad (1)$$

In Eq. (1),  $\lambda$ ,  $P(\lambda)$  and  $\phi(\lambda)$  correspond to the wavelength, the solar spectrum of AM1.5 and the conversion efficiency of the cell, respectively. Since the photocurrent generated in the  $\text{TiO}_2$  film is in the range of 300–550 nm, the calculated  $J_{\text{dye}}$  is attributed only to the photoresponse of Ru-dye, and  $J_{\text{Ag-dye}}$  to that of Ag-assisted Ru-dye. The value of  $J_{\text{dye}}$  is considered to be proportional to the quantity of adsorbed Ru-dye on the  $\text{TiO}_2$  thin films, because the increase of the density of adsorbed dye should result in the increase of photocurrent density.

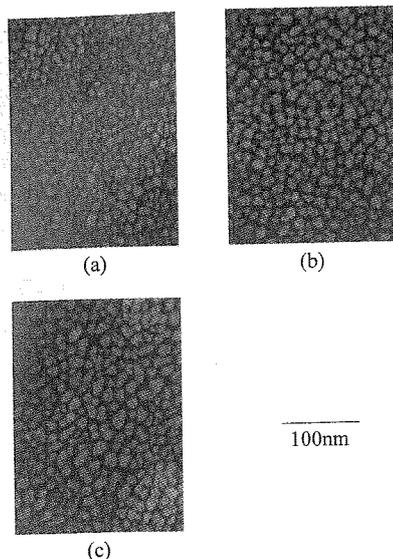


Fig. 4 SEM images of Ag nanoparticles deposited on dye-adsorbed TiO<sub>2</sub> films at different Ru-dye concentrations. The values of  $J_{\text{dye}}$  of cells fabricated from each film are (a) 0.53 (b) 2.7 (c) 3.7  $\mu\text{A}/\text{cm}^2$ , respectively

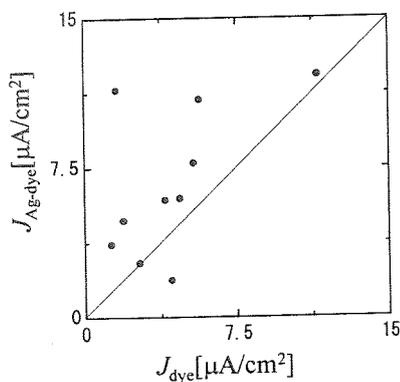


Fig. 5 Calculated photocurrent density of Ru-dye-sensitized cells with and without Ag using action spectra with the UV light

In Figure 4, FE-SEM pictures of evaporated Ag particles on dye-adsorbed TiO<sub>2</sub> at different Ru-dye concentrations are shown. The value of  $J_{\text{dye}}$  calculated for each film is (a) 0.53, (b) 2.7 and (c) 3.7  $\mu\text{A}/\text{cm}^2$ , respectively.

$J_{\text{Ag-dye,dye}}$  in Figure 5 show the calculated photocurrent density with and without Ag, respectively, using the measured action spectra under the excitation of UV light.

Figure 6 shows the photocurrent density of cells with and without Ag measured under illumination by an AM1.5 light with a UV cut filter (under 400 nm).

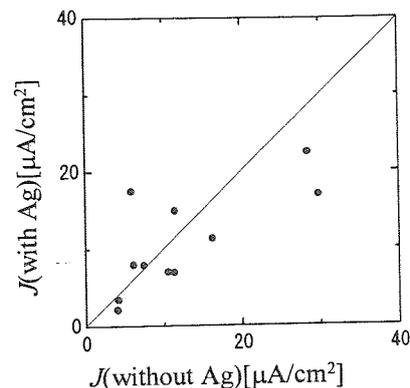


Fig. 6 Measured photocurrent density of Ru-dye-sensitized cells with and without Ag under illumination by the AM1.5 light equipped with a UV cut filter (under 400 nm)

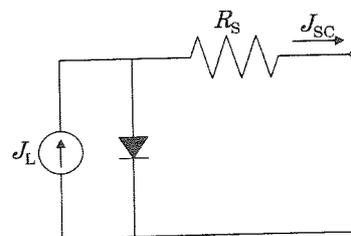


Fig. 7 Equivalent circuit of solar cells with a serial resistance

### 3. Discussion

Generally, the short-circuit photocurrent density  $J_{\text{sc}}$  of solar cells with serial resistance (Figure 7) is written as

$$J_{\text{sc}} = J_L - J_0 \left[ \exp\left(\frac{qR_s J_{\text{sc}} S}{nkT}\right) - 1 \right] \quad (2)$$

where  $J_L$  is the constant current density,  $J_0$  is the dark current density,  $q$  is the electronic charge,  $R_s$  is the serial resistance, and  $S$  is the surface area of the cell.  $J_{\text{dye}}$  and  $J_{\text{Ag-dye}}$  in our cells can be written as below.

$$J_{\text{dye}} = J_{L,\text{dye}} - J_{0,\text{dye}} \left[ \exp\left(\frac{qR_s J_{\text{dye}} S}{nkT}\right) - 1 \right] \quad (3)$$

$$J_{\text{Ag-dye}} = J_{L,\text{Ag-dye}} - J_{0,\text{Ag-dye}} \left[ \exp\left(\frac{qR_s J_{\text{Ag-dye}} S}{nkT}\right) - 1 \right] \quad (4)$$

In the case of our cells,  $J_{L,dye}$  is a function of the dye concentration. When the photocurrent of cells with Ag is enhanced by the surface plasmon resonance,  $J_{L,Ag-dye}$  in Eq. (4) is enhanced compared to  $J_{L,dye}$  in Eq. (3).

As shown in Figure 3, the photocurrent of Ru-dye-sensitized cells is remarkably increased in the existence of Ag nanoparticles at lower concentrations of adsorbed Ru-dye. It is considered that the increase of the photocurrent with Ag nanoparticles is attributed to the increase of the optical absorption of dye, and resulting in the photocurrent enhancement by the effect of the surface plasmon resonance of Ag and/or the internal photoemission from Ag. Concerning the internal photoemission from Ag, the photocurrent attributed to it should be decreased with the increase of adsorbed dye, because the charge transfer of the carriers to  $TiO_2$  generated in Ag nanoparticles should be prevented by the increase of dye molecules between Ag and  $TiO_2$ . That is why the enhancement is attributed to the effect of the surface plasmon resonance in this case. Figure 3 also shows that the photocurrent of the cells with Ag is nearly proportional to that of the cells without Ag. In Figure 4, Ag nanoparticles at different adsorbed-dye concentrations show almost the same size, shape and density. Accordingly, the enhancement of the local electromagnetic field near Ag should be the same on dye-adsorbed  $TiO_2$  films at different dye concentrations and the increase of the photocurrent per dye molecule should be constant. That is why the rate of the increase is constant at lower dye concentrations. It is considered that the second terms of the right sides of Eqs. (3) and (4) are negligible at lower dye concentrations which corresponds to lower photocurrent densities, and the  $J_{L,Ag-dye}$  in Eq. (4) is enhanced and proportional to  $J_{L,dye}$  in Eq. (3). Figures 5 and 6 show a similar tendency as Figure 3 at lower Ru-dye concentrations.

The photocurrent of Ru-dye-sensitized cells decreases with Ag nanoparticles at higher Ru-dye concentrations as shown in Figure 3. While there is surface plasmon resonance which increases the photocurrent with Ag as described above, two effects are given as the reasons for the decrease of the photocurrent with Ag nanoparticles. One is the increase of the density of traps on the surface that increases the recombination rate of generated carriers, and the other is the increase of fluctuations of the conduction band of  $TiO_2$  that retards the migration of the carriers from the surface to the interior of  $TiO_2$  (Nakato and Tsubomura, 1985; Nakato *et al.*, 1988). Since these negative effects are dominant at higher dye concentrations, compared with lower concentrations, the photocurrent of Ag deposited cells decreases. It means that the positive effects decrease or the negative effects increase at higher concentrations. As seen in Figure 4, the structure of Ag nanoparticles is similar at different Ru-dye concentrations, and the enhancement

effect of the surface plasmon resonance is not varied with the dye concentration in our cells. Therefore, negative effects are the reasons for the decrease of the photocurrent with Ag nanoparticles. It means that  $J_{0,Ag-dye}$  in Eq. (4) increases compared to  $J_{0,dye}$  in Eq. (3), and the second term in Eq. (4) is not negligible at higher Ru-dye concentrations. This indicates that the increased trap levels and band-edge fluctuations dominate and cause the decrease of the photocurrent at higher dye concentrations. Even if the optical absorption is enhanced by the surface plasmon resonance, it would not increase the photocurrent at higher dye concentrations. Thus, it is important to control the structure and the quantity of Ag nanoparticles for the application of the surface plasmon resonance effect on dye-sensitized solar cells.

We can see a little increase of the photocurrent of the cells with Ag nanoparticles at higher dye concentrations in Figure 5, which means the increase of the photocurrent with UV light illumination. Since the UV light was illuminated from the side of the  $TiO_2$  film electrode in our experiments, it was absorbed by the  $TiO_2$  film and the conductivity of the film was enhanced by photons generated by the UV light. It corresponds to the theoretical expectation that the decrease of the photocurrent is suppressed by the decrease of the serial resistance as in Eq. (4).

Among Figures 3, 5 and 6, we can observe that the decrease of the photocurrent with Ag nanoparticles at higher Ru-dye concentrations is largest in Figure 3, and is smallest in Figure 5, although the data contain some errors in the figures that may be caused by the  $TiO_2$  electrode. We can explain this tendency with the difference of the effect of UV light illumination. The UV light is not illuminated at all in the case of Figure 3, is illuminated a little (over 400 nm) in the case of Figure 6, and is strongly illuminated by an Hg lamp in the case of Figure 5. However, the negative effects due to the increased trap levels and band-edge fluctuations are dominant at higher dye concentrations even under UV light excitation, because the increase of the photocurrent of cells with Ag nanoparticles at higher dye concentrations is much smaller than that at lower dye concentrations in Figure 5.

## Conclusions

We investigated the photocurrent of Ru-dye-sensitized solar cells with and without Ag at different Ru-dye concentrations. At lower Ru-dye concentrations, the photocurrent with silver was enhanced dramatically by the effect of the surface plasmon resonance of Ag nanoparticles. On the other hand, the photocurrent with silver was decreased at higher Ru-dye concentrations. The decrease of the photocurrent is attributed to the increased trap levels and band-edge fluctuations caused by Ag incorporation. These results

suggest that the enhancement of the photocurrent can be achieved only under the condition that the increases of trap levels and band-edge fluctuations are suppressed, although the surface plasmon resonance effect can enhance the optical absorption of Ru-dye. Therefore, the structure and the quantity of Ag particles is very crucial for the application of the surface plasmon resonance effect to dye-sensitized solar cells.

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