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Electron-hole recombination via reactive intermediates formed on PdO-doped $SrTiO_3$ electrodes. Estimation from comparison of photoluminescence and photocurrent

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Abstract

We measured photoluminescence of PdO-doped $SrTiO_3$ electrodes, whose photoelectrochemical properties are similar to those of non-doped $SrTiO_3$ electrodes. Photocurrent due to oxidation of water on PdO-doped and non-doped $SrTiO_3$ electrodes started at a potential about 0.1 V more positive than the flat-band potential. When 2-propanol was added to the solution, the photocurrent started at the potential close to the flat-band potential and the current-doubling effect was observed due to the oxidation of 2-propanol. The PdO-doped $SrTiO_3$ electrodes showed red photoluminescence by band gap excitation. The emission intensity or its potential dependence was not affected by addition of 2-propanol to the solution. In the solution containing 2-propanol, the photoluminescence-voltage curve was found to be almost complementary to the photocurrent-voltage curve observed. On the other hand, when they were measured in a solution without 2-propanol, there was a potential region where both photocurrent and photoluminescence were low. These results suggested that electron-hole recombination occurs via intermediates of the oxidation of water, while the recombination is very scarce when 2-propanol is oxidized on the electrode.

Keywords: Electron-hole recombination; PdO-doped $SrTiO_3$ electrodes; Photoluminescence; Photocurrent; Photocatalyst; 2-Propanol

1. Introduction

Photoluminescence of semiconductor electrodes can be a good method for investigating the electron-hole recombination process in the bulk of the electrodes. As the semiconductor electrodes for these studies, cadmium sulfide or related materials have been extensively studied [1–6]. Streckert et al. [1] analyzed the competitive relationship between the charge separation leading to photoelectrochemical reactions and charge recombination leading to photoluminescence.

From the viewpoint of utilization of semiconductors to solar energy conversion and environmental applications, titanium dioxide and some oxide semiconductors are more important than cadmium sulfide [7–10]. However, the photoluminescence of these oxide semiconductors have not been widely studied, because their photoluminescence is very weak. Photoluminescence from oxidation intermediates of water formed on TiO_2 has been observed at 840 nm by Nakato et al. [11,12]. Electrochemiluminescence from metal-ion doped $SrTiO_3$, which showed photoresponse to visible light, has been investigated to determine the energy levels unique to the dopants [13].

Among the fates of the charge carriers photogenerated in the semiconductors, surface recombination is an essential path determining the efficiency of the photoelectrochemical and photocatalytic reactions. This process is especially important in semiconductor photocatalysts, because they have large surface areas and operate near the flat-band conditions. We consider that useful information about the surface recombination process can be obtained from comparison of photoluminescence and photocurrent. In order to clarify the effect of the surface recombination process on oxide semiconductors, we used PdO-doped $SrTiO_3$ electrode, which shows strong red emission [13].

2. Experimental

2.1. Materials and preparation of PdO-doped $SrTiO_3$ electrodes

$SrTiO_3$ powder was obtained from Fuji Titanium Industry. Guaranteed-grade palladium(II) oxide (PdO) was

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obtained from Wako Pure Chemicals. All other chemicals used in the experiments were purchased from commercial sources as guaranteed-grade reagents and used without further purification.

In order to make PdO-doped $SrTiO_3$, PdO particles were loaded on $SrTiO_3$ particles by grinding $SrTiO_3$ powder (2.0 g) with 0.01–0.06 wt.% PdO powder in an agate mortar. The mixed powder was pressed into disks 1 cm in diameter and sintered at 1400°C for 2 h. After the surface layers of the disks were removed by polishing with sandpaper, the disks were heated in a stream of hydrogen at 1100°C for 1 h so as to gain electrical conductivity. The electrodes for photoelectrochemistry were fabricated by connecting copper wire to the back surface of the $SrTiO_3$ crystals via a Ga–In alloy.

2.2. Electrochemical and photoluminescence measurements

The electrochemical measurements were carried out in aqueous solutions containing 0.1 M ($M = mol\,dm^{-3}$) H_2SO_4 under potentiostatic conditions using a potentiostat (Nikkokeisoku, NPOT-2501) and an Ag/AgCl reference electrode, and a platinum plate counter electrode. In some experiments, 2-propanol (25% in volume) was added to the aqueous solutions. A 500 W high-pressure mercury lamp (Wacom, BMO-500DY) was used as a light source. The light beam was passed through a Pyrex glass filter to cutoff wavelengths shorter than 300 nm, and through fine stainless-meshes to adjust the irradiation intensity.

Photoluminescence of the PdO-doped $SrTiO_3$ electrodes was measured in aqueous solutions of 0.1 M H_2SO_4 under the same conditions as the electrochemical measurements. 2-propanol (25% in volume) was added to the aqueous solutions in some experiments. The PdO-doped $SrTiO_3$ sintered electrodes were illuminated at 355 nm and photoluminescence spectra were recorded using a Hitachi F4500 fluorescence spectrophotometer.

3. Results and discussion

3.1. Photocurrent at PdO-doped $SrTiO_3$ sintered electrodes

The I–V characteristics of non-doped $SrTiO_3$ electrodes have previously been studied in detail [14–16]. The photoelectrochemical properties of $SrTiO_3$ electrodes are similar to those of TiO_2 electrodes, although the onset potential of photocurrent shifts toward negative potential by about 0.3–0.35 V [14,15]. Both $SrTiO_3$ and TiO_2 electrodes are important, because they are chemically stable and capable of oxidizing water under UV irradiation.

The electrochemical properties of PdO-doped $SrTiO_3$ electrodes we prepared were essentially the same as the non-doped $SrTiO_3$ electrodes, unless the doping concentration was very high. Fig. 1 shows the current-voltage characteristics of a PdO-doped $SrTiO_3$ electrode under UV irradiation in an aqueous solution of 0.1 M sulfuric acid. When 2-propanol (25% in volume) was added to the solution, photocurrent started at a lower potential, and the saturation current is enhanced by about 1.5-times, as show by a solid line in Fig. 1. The enhancement of the current is attributed to the electron injection from the intermediate of the oxidation of 2-propanol to the conduction band of semiconductor electrodes, and has been called a current-doubling effect [17–20]. These suggest that 2-propanol are photo-oxidized more easily than water on the PdO-doped $SrTiO_3$ electrode as the case of TiO_2 electrode [18].

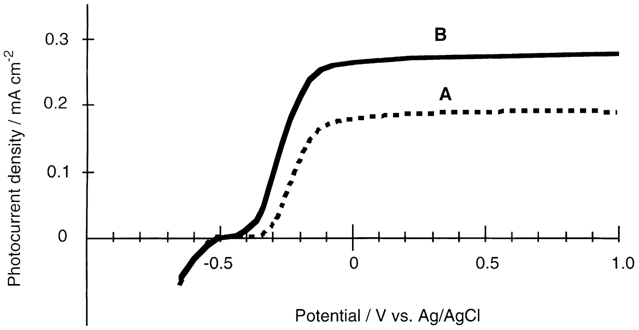

Fig. 1. Photocurrent-voltage characteristics of a PdO(0.01 wt.%)-doped $SrTiO_3$ electrode measured in 0.1 M H_2SO_4 (A), and in 0.1 M H_2SO_4 containing 2-propanol (25% in volume) (B).

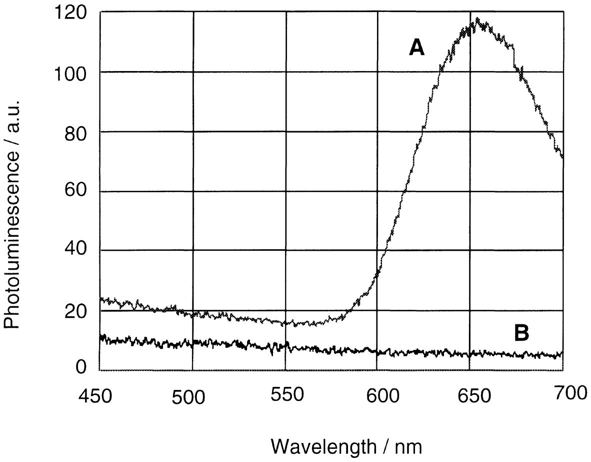

Fig. 2. Photoluminescence spectra of PdO(0.01 wt.%)-doped $SrTiO_3$ electrode (A) and non-doped $SrTiO_3$ electrode (B) measured in 0.1 M H_2SO_4 under open circuit conditions at room temperature. Excitation wavelength is 355 nm.

3.2. Photoluminescence of the PdO-doped $SrTiO_3$ electrode

Photoluminescence spectra of PdO-doped $SrTiO_3$ and non-doped $SrTiO_3$ sintered electrodes were measured in a 0.1 M H_2SO_4 solution under open circuit conditions. As seen in Fig. 2, the PdO-doped $SrTiO_3$ electrode showed red photoluminescence with a peak at 660 nm. The spectrum is almost the same as the electrochemical luminescence

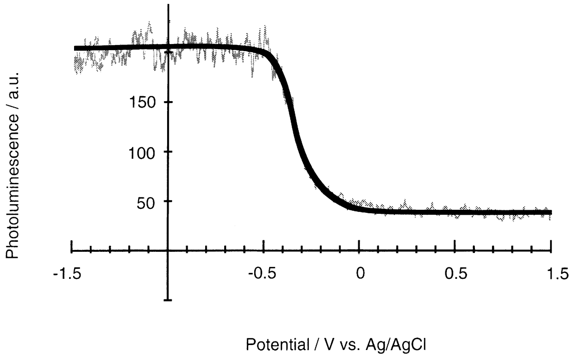

Fig. 3. Photoluminescence intensity of PdO(0.01 wt.%)-doped $SrTiO_3$ electrode versus electrode potential. Photoluminescence was monitored at 660 nm in 0.1 M H_2SO_4 by photoexcitation at 355 nm.

of the PdO-doped $SrTiO_3$ electrode measured in alkaline solutions of $Na_2S_2O_8$ [13]. The same photoluminescence spectra were obtained when measured in air. On the other hand, practically no photoluminescence was observed with the non-doped $SrTiO_3$ electrode. These results suggests that PdO or Pd ion incorporated into the bulk of $SrTiO_3$ grains generates emissive electron-hole recombination centers.

The intensity of the photoluminescence increased with lowering potential and leveled off at the potential about −0.6 V versus Ag/AgCl, as seen in Fig. 3. This potential is similar to the flat-band potential of $SrTiO_3$ [14]. The photoluminescence intensity also levels off at a low level at potentials more positive than 0 V. This potential independent photoluminescence is attributable to the emission from PdO-doped $SrTiO_3$ grains electrically isolated from the other parts of the sintered body.

In contrast to the case of the photocurrent, the photoluminescence intensity and its potential dependence were not affected by adding 2-propanol to the aqueous solution.

3.3. Estimation of electron-hole recombination via oxidative intermediates of water on $SrTiO_3$

We found that, when measured in solutions containing 2-propanol, the photocurrent-voltage and the photoluminescence-voltage curves are almost complementary each other. The relationship between them is shown in Fig. 4a. Note that the potential independent photoluminescence, which was observed at potentials more positive than 0 V (see Fig. 3), is subtracted.

When we compared the relationship between the photoluminescence and photocurrent measured in the solution without 2-propanol, there is a potential region where both photocurrent and photoluminescence are low, as seen in Fig. 4b. The deficient component is shown by a solid line in the figure. The solid line in this figure is drawn so as to make the sum of this component, photocurrent, and photoluminescence becomes unity at every electrode potential. Similarly, this component is drawn in Fig. 4a for the case where water is oxidized. In this case, this component is very small.

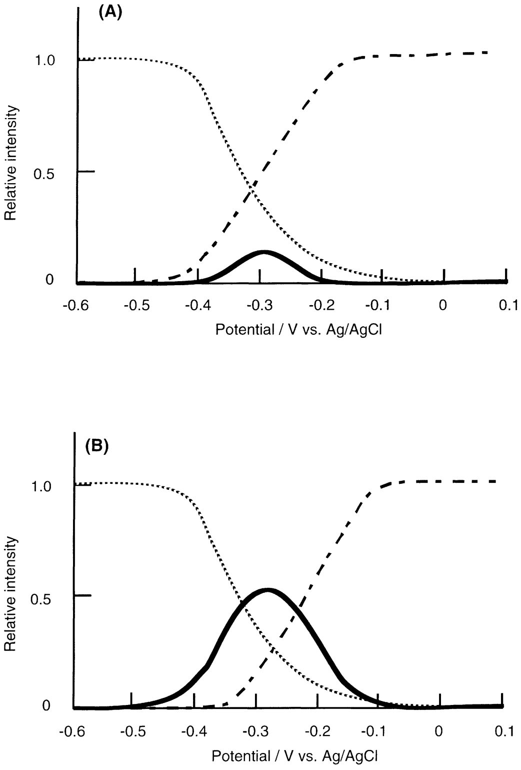

Fig. 4. Estimation of electron-hole recombination on the surface of $SrTiO_3$ in 0.1 M H_2SO_4 containing 2-propanol (25% in volume) (A), and in 0.1 M H_2SO_4(B). The surface recombination (——) was determined from the comparison of photoluminescence (- - -) and photocurrent (— - —) properties. The saturated values of photoluminescence and photocurrent are normalized, and the intensity of photoluminescence observed at voltages more positive than 0 V versus Ag/AgCl (see Fig. 3) is subtracted.

The photoluminescence of the doped and non-doped semiconductors is usually proportional to the rate of electron-hole recombination in the bulk [4]. It is, therefore, reasonable to think that the sum of the components of photocurrent and photoluminescence is unity, if chemical reactions and recombination in the bulk are the only competitive processes in photoirradiated semiconductor electrodes. The third component, as shown by the solid lines in Fig. 4, suggests the presence of another recombination process. The large difference in the intensities of this component between the results obtained in the solutions with and without 2-propanol suggests that the electron-hole recombination takes place via the reaction intermediates generated on the surface of the electrode.

As discussed above, the oxidative intermediate of 2-propanol is chemically unstable and simultaneously oxidized to acetone by releasing electrons. This means that the life of the intermediate is short and that the possibility of the recombination via this intermediate is very low. On the other hand, for the oxidation of water, at least four electrons must be removed to produce one oxygen molecules. This leads to the accumulation of reaction intermediates on the electrode surface, and enhanced electron-hole recombination in the potential region near the flat-band potential.

The electron-hole recombination process via the reaction intermediates on semiconductors is especially important for semiconductor-particulate photocatalysts, because large band bending is hardly generated in fine particles [21]. This probably is the main reason for the difficulty of oxidation of water on many semiconductor photocatalysts. We have previously found that the oxidation of water on photoirradiated TiO_2 particles is largely accelerated by addition of Fe(III) ions to solutions [22,23]. It was also found that the photocurrent at the TiO_2 electrode was improved near the flat-band potential, when Fe(III) ions were adsorbed on the TiO_2 electrode [22,23]. Such effects by adsorbed Fe(III) ions are considered to arise from the change of the intermediate species of the oxidation of water on TiO_2 surface. The comparison between photocurrent and photoluminescence will give us important information about the recombination process via the reaction intermediates on the semiconductor electrodes.

4. Conclusions

We have demonstrated a new method of estimating electron-hole recombination via the reaction intermediates on semiconductor electrodes from the comparison of photocurrent-voltage and photoluminescence-voltage curves using luminescent $SrTiO_3$ electrodes. This recombination process is especially important for the semiconductor photocatalysts, because they operate near the flat-band potential. The method will be useful in understanding their mechanisms.

Acknowledgements

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