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Effect of steam treatment on photocurrent and dye–titania interaction in dye-doped titania gel

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Abstract

Thin titania-gel films containing dispersed fluorescein or alizarin were prepared by the sol–gel method and treated with steam in order to promote crystal growth of the titania particles. The incident photon to current efficiency (IPCE) value and the quantum efficiency of the photocurrent generation increased with an increase in the steam-treatment duration of the fluorescein-doped films. The quantum efficiency was improved by 14 times after 12-h steam treatment. The growth and crystallization of the titania particles by the steam treatment improved their electric conductivity. On the other hand, the photocurrent only slightly changed and the crystal slightly grew by the steam treatment in the alizarin-doped films. Alizarin molecules prevented the crystal growth of the titania gel due to their strong interaction with Ti around them.

Keywords: Photocurrent; Dye-doped titania gel; Sol–gel method; Steam treatment; Crystal growth

1. Introduction

Energy conversion properties of dye-sensitized solar cells based on titania are being actively investigated all over the world. The conversion efficiency has attained more than 10% [1–3]. In a conventional method to prepare electrodes for a dye-sensitized solar cell, an organic dye is adsorbed onto the film. The titania films can be easily prepared by the sol–gel method, i.e., dip-coating the materials in a sol of titanium alkoxide and heating them at 400–500 °C. It is important to study new dye-sensitized titania systems prepared in a different concept from the conventional procedures for the further development of such solar cells. In our original investigation, the dye-doped titania-gel films were prepared by a simple sol–gel process such that the materials are dip-coated in a sol including an organic dye without the normal heating process [4]. This method allows the dye molecules to be dispersed into the network of the titanium polymer compounds at a molecular level. The preparation of titanium dioxide at low temperature using a wet process, such as the sol–gel method, has also been widely investigated because of the advantages of uniform nanoparticle formation and saving energy [5–14]. The following two advantages are expected in our preparation method of the electrode compared with the conventional samples: one is that the higher dispersion of the dye into the titania gel can improve the efficiency of light absorption. The other is that the higher contact area between the dye and titania can improve the efficiency of the electron transfer. However, the electric conductivity is very low in the unheated titania gel due to the high number of defects [4]. Treatment of the titania gel at low temperature is required in order to improve the conductivity of the gel without dye decomposition. A hydro- or solvo-thermal treatment at around its boiling point is expected to be effective in promoting the condensation and crystallization of the gel [6,9,12–14].

In our previous study [4], a photocurrent was observed in the fluorescein-doped titania-gel films during visible light irradiation. The photocurrent results from the electron transfer from the excited state of the entrapped dye to the conduction band-like states of the titania gel. An anatase-type crystal was produced by the steam treatment of the titania gel. The photocurrent value increases with the duration of the steam treatment because the crystallization of the titania gel increases its electric conductivity.

Organic dye molecules, such as rhodamine B [15,16] and methylene blue [17], tend to be separately encapsulated into the pores of the sol–gel reaction systems of silicon alkoxide as the

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reaction proceeds. On the other hand, rhodamine B molecules tend to be aggregated in the sol–gel reaction systems including titanium alkoxide as the reaction proceeds [18], because of the strong interaction between the dye molecules and the TiOH groups [19]. It is important for energy conversion in the dye-sensitized solar cell to clarify the bonding and donor–acceptor interaction between the dye molecules and the titania matrix [20–26]. Developing such systems promises not only to improve the solar cell efficiency, but also to provide new application devices using other photofunctional materials. Furthermore, the investigation of this interaction allows determining new knowledge which is expected to be applicable to conventional solar systems from a different viewpoint. In this study, the thin titania-gel films containing dispersed fluorescein or alizarin were prepared by the sol–gel method and treated with steam. The incident photon to current efficiency (IPCE) and quantum efficiency of the photocurrent in the electrodes were observed as a function of the steam-treatment duration. Alizarin is expected to strongly interact with Ti and has been well-studied as a sensitizer for titania [27–31]. Therefore, alizarin is suitable to compare with fluorescein due to their difference in the coordination properties. This paper describes the steam-treatment effect on the properties of the light-to-electric conversion in the dye-doped titania-gel film and discusses the interaction between the dye and the titania.

2. Experimental

2.1. Preparation of electrodes

Titanium tetraisopropoxide, ethanol, fluorescein, alizarin, hydrochloric acid, diethylene glycol, iodine, and lithium iodide (Wako Pure Chemicals, S or a regent grade) were used without further purification. Water was ion-exchanged and distilled. Glass plates coated with the ITO transparent electrode (Yamakyu Tokushu Glass) were soaked in hydrochloric acid ($1.0\,\mathrm{mol\,dm^{-3}}$) for 1 h and then rinsed with water. The electrolyte for the electrical measurement consisted of a diethylene glycol solution of iodine ($5.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) and lithium iodide ($0.50\,\mathrm{mol\,dm^{-3}}$).

The sol–gel reaction system was prepared by mixing $15.0\,\mathrm{cm^3}$ of titanium tetraisopropoxide, $15.0\,\mathrm{cm^3}$ of the ethanol solution of fluorescein or alizarin (1.0–$5.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$), and $8.0 \times 10^{-2}\,\mathrm{cm^3}$ of hydrochloric acid ($1.0 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) as the catalyst of the sol–gel reaction. A system without the dye was also prepared. Since it took 90–100 days for gelation of these systems, our dip-coating had been performed before the gelation to prepare a titania-gel film on a glass plate coated with the ITO transparent electrode. The dip-coated thin films were made from the sol–gel systems reacting for 50 days to prepare the electrodes in this study.

In order to prepare the electrode samples coated with crystalline titania, the glass plates with the ITO transparent electrode were dip-coated with the dye-free system and then heated at 500 °C for 1 h. Furthermore, some of these electrodes were coated with the sol–gel system including the fluorescein or alizarin dye.

The conventional dye-sensitized electrode was also prepared in order to compare them with our original samples. The powdered titania (Nippon Aerosil, P25), 6.0 g, was dispersed in a mixture of $10.0\,\mathrm{cm^3}$ of water, $0.20\,\mathrm{cm^3}$ of acetylacetone (Wako Pure Chemicals, S grade), and $0.05\,\mathrm{cm^3}$ of 20% aqueous solution of polyoxyethylene(10)octylphenylether (Triton X-100, Wako Pure Chemicals, reagent grade) using a planetary ball mill (Retsch PM200). The resulting paste was spread on the glass plate with the ITO transparent electrode and heated at 450 °C for 30 min. The electrode sample was soaked in an ethanol solution of fluorescein ($1.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$) for 24 h.

2.2. Measurements

The UV–visible absorption spectra of the prepared electrode samples were observed using a spectrophotometer (Shimadzu UV-2500). The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the counter ITO electrode. Visible lights of wavelengths longer than 400 nm obtained from a fluorescence spectrophotometer (Shimazdu RF-5300) with a 150 W Xe short arc lamp (Ushio) were irradiated on the electrodes for the spectroscopy. Under light irradiation, the short circuit currents of the electrodes were measured by an electrometer (Keithley model 617). The crystalline phase was determined using a X-ray diffractometer (Rigaku RINT-2200V). Potassium ferrioxalate actinometry was carried out in order to estimate the IPCE and quantum efficiency for the photocurrent from the excited dye in the electrode samples. The intensity of the light source was determined to be 1.15×10^{-8} einstein/s at 334 nm. The intensity at each wavelength of the light source was obtained from its radiation spectrum supplied by the lamp maker.

2.3. Steam treatment

The steam-treatment effect on the UV–visible absorption and photocurrent spectra of the electrode samples was investigated. Water was heated at 100 °C and the electrode samples were exposed to its steam for 1–18 h. The pressure of the steam was about 100 kPa.

3. Results and discussion

3.1. Photocurrent of fluorescein-doped electrodes

Fig. 1 shows the visible absorption and IPCE spectra of the fluorescein-doped titania-gel film untreated and steam-treated for 3–18 h. The untreated film exhibits the visible absorption spectrum that is located around 480 nm and ranging over longer wavelength than that observed in solvents. This result indicates that main fluorescein species were the anion (at around 450–480 nm) and some fluorescein molecules existed as the dianion (at around 490 nm) [32]. In addition, the longer wavelength band indicates that a small amount of fluorescein molecules formed the dianion-like species resulting from the strong interaction and an ester-like linkage between the carboxyl group of the anion and the TiOH group [22,23,32–34].

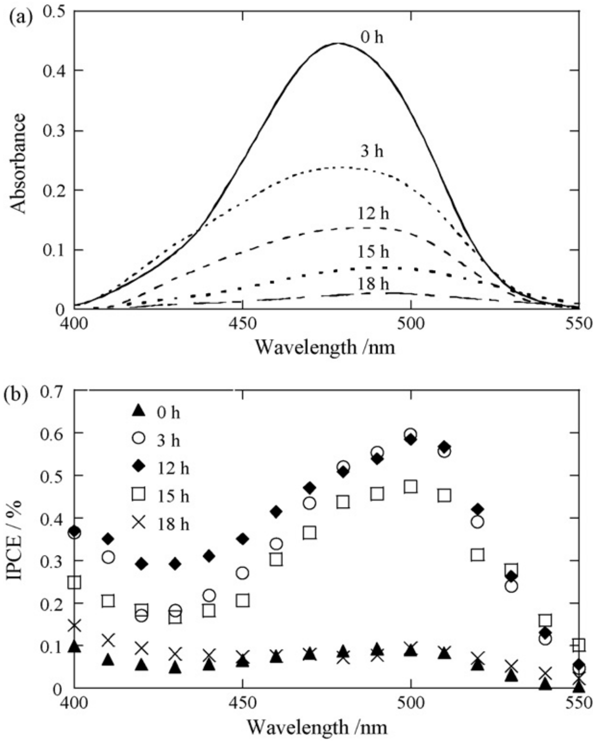


Fig. 1. Changes in (a) visible absorption spectra and (b) IPCE spectra of the fluorescein-doped titania-gel film by the steam treatment for 0, 3, 12, 15, and 18 h.

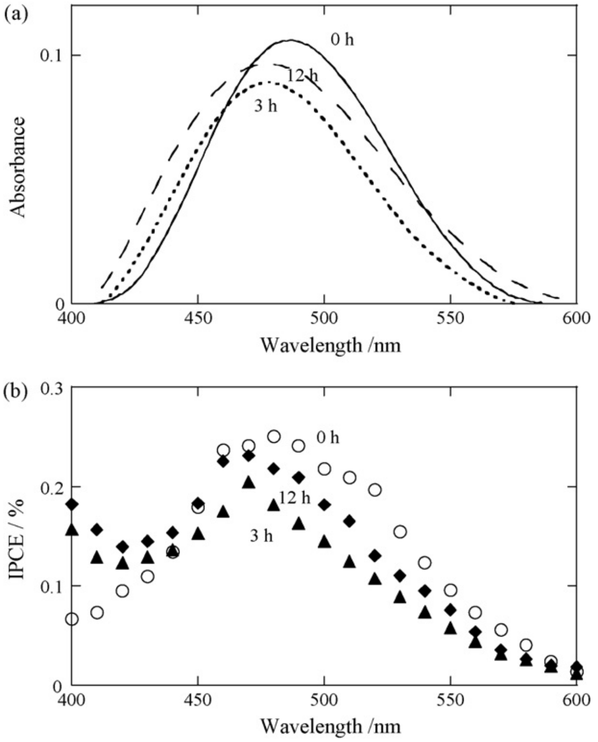


Fig. 2. Changes in (a) visible absorption spectra and (b) IPCE spectra of the alizarin-doped titania-gel film by the steam treatment for 0, 3, and 12 h.

The absorbance decreased and the spectral peak of the film was red-shifted from around 480–485 nm with an increase in the steam-treatment time [4]. These results indicate that the anion was preferentially desorbed from the inside of the titania-gel film because the species was weakly trapped in the pores of the gel.

The changes in the IPCE spectra of the fluorescein-doped titania-gel film by the steam treatment are shown in Fig. 1b. Some of these values were estimated from the photocurrent data reported in a previous paper [4]. In spite of the absorbance decrease, the photocurrent of the electrode increased with an increase in the treatment time until while the peak at around 500 nm was only slightly changed. The results suggest that the increase in the IPCE values is due to electric conductive improvement of the titania gel and the dianion-like species plays an important role in generating the photocurrent in this system. The IPCE values were almost constant after the 3–12 h steam treatment and then decreased after 15 h due to further dye desorption.

3.2. *Photocurrent of alizarin-doped electrodes*

Fig. 2 shows the changes in the visible absorption and IPCE spectra of the alizarin-doped titania-gel film versus the steam-treatment time. The absorption spectrum observed before the steam treatment (0 h) exhibits a peak at around 490 nm. The absorbance hardly decreased and the spectral peak was blue-shifted to around 480 nm by the steam treatment. This slight spectral shift indicates the structural change of alizarin by the electrostatic change in the titania [31,35]. It is suggested, for example, the pH-dependent change from the 2,9- to 9,10-antraquinoid structure because the absorption peaks of the metal complex with their anion are 500–515 and around 460 nm, respectively [35]. For the fluorescein-doped films, the dye molecules were transferred to the water and the absorbance decreased by 25% during the 12-h steam treatment. The slight decrease in the absorbance of alizarin indicates that the strong interaction between alizarin and Ti prevents dye desorption from the sample surfaces and only a small amount of alizarin molecules were transferred to the water. The slight increase in the absorbance of alizarin after the 12-h steam treatment is suggested to be due to an increase in the amount of the 9,10-antraquinoid complex with the structural change of alizarin instead of the dye desorption. As expected, the photocurrent slightly decreased and the spectra were slightly blue-shifted similar to the absorption spectra. The IPCE value of the non-treated alizarin sample is higher than that of the fluorescein sample due to the stronger interaction with Ti. However, no remarkable increase was observed as seen in the fluorescein-doped samples.

3.3. *Dependences of dye concentration on photocurrent and XRD patterns of fluorescein- and alizarin-doped electrodes*

The dye concentration dependences of the visible absorption and IPCE spectra of the fluorescein- and alizarin-doped titania-gel films were investigated. The absorbance and IPCE values of the dye-doped films before the steam treatment were proportional to their concentration although these results are not shown. Fig. 3 shows the results of the fluorescein-doped samples at the

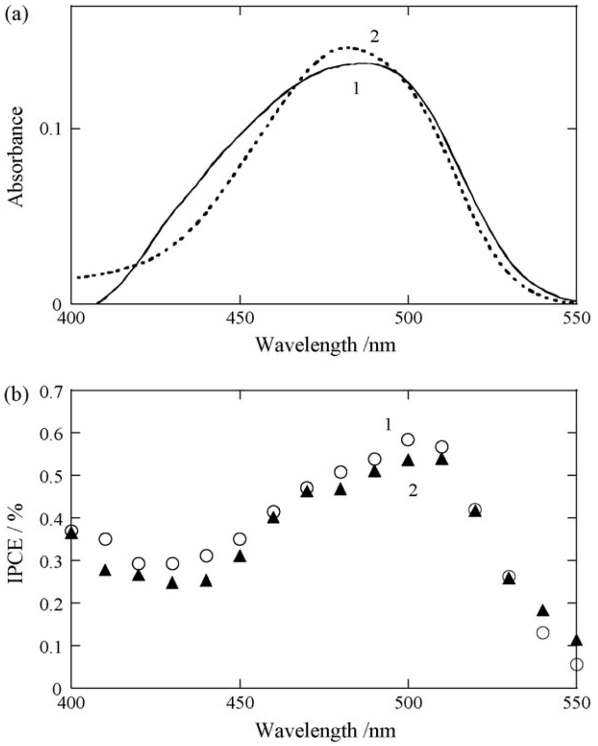


Fig. 3. (a) Visible absorption spectra and (b) IPCE spectra of the fluorescein-doped titania-gel films steam-treated for 12 h. The films were prepared from the sol–gel precursor solutions containing (1) 1.0 and (2) 3.0×10^{-2} mol dm^{-3} fluorescein.

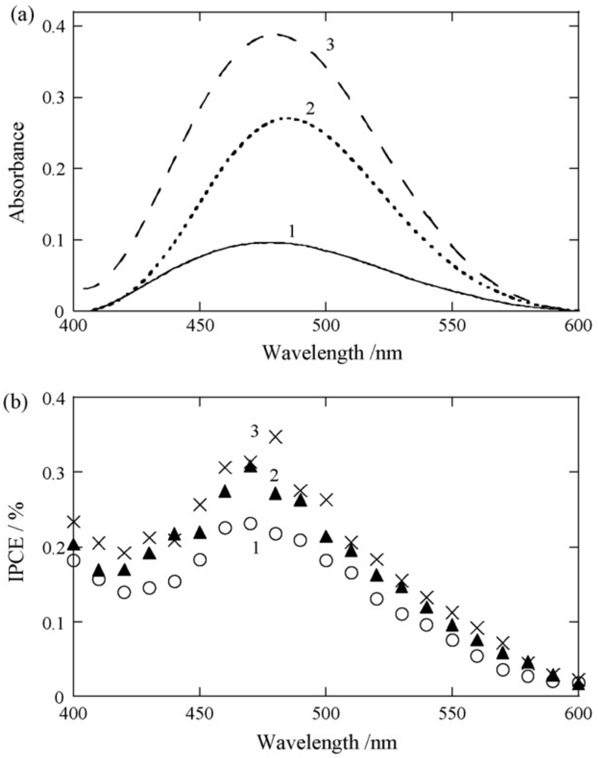


Fig. 4. (a) Visible absorption spectra and (b) IPCE spectra of the alizarin-doped titania-gel films steam-treated for 12 h. The films were prepared from the sol–gel precursor solutions containing (1) 1.0, (2) 3.0, and (3) 4.0×10^{-2} mol dm^{-3} alizarin.

concentration of 1.0 and 3.0×10^{-2} mol dm^{-3} after the 12-h steam treatment. Both the absorbance and IPCE values in the fluorescein-doped film did not almost depend on dye concentration. This result is because a certain amount of the dye molecules remained in the films regardless of the concentration after the dye desorption into the water by the steam treatment. The dye concentration dependences of the visible absorption and IPCE spectra of the alizarin-doped titania-gel film steam-treated for 12 h are shown in Fig. 4. Unlike the fluorescein-doped samples, both the absorbance and IPCE values in the alizarin-doped films somewhat increased as a function of dye concentration. The absorbance of alizarin in the films is proportional to its concentration in the sol–gel precursor solutions. This result indicates that only a small amount of alizarin molecules were desorped into the water by the steam treatment because the strong interaction between alizarin and Ti prevents the dye desorption. However, the IPCE value of the film did not increase as much as the absorbance increased with alizarin concentration.

The dye concentration dependence of the XRD patterns of the fluorescein- and alizarin-doped titania-gel films steam-treated for 12 h was examined and shown in Fig. 5 [4]. These concentrations denote those in the sol–gel precursor solutions. The patterns of the fluorescein samples were independent of its concentration and the results of the samples at the concentration of 1.0 and 3.0×10^{-2} mol dm^{-3} are shown. These patterns are similar to those of the dye-free titania-gel films steam-treated for 3–12 h, which were reported in previous paper [4]. The peak at around 25° appeared in the XRD pattern of the sample treated with steam for 1 h and it became sharp with the treatment time. These results mean that a small anatase-type crystal was formed after the 1-h treatment and the crystal grew by further treatment. The independence of the dye concentration is due to the desorption of a large amount of dye molecules during the steam treatment. The pattern of the alizarin sample at the concentration of 1.0×10^{-2} mol dm^{-3} is broader after even the 12-h steam treatment than that of fluorescein. The patterns of the alizarin

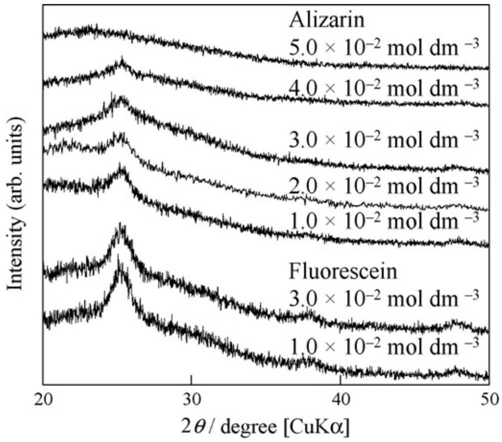
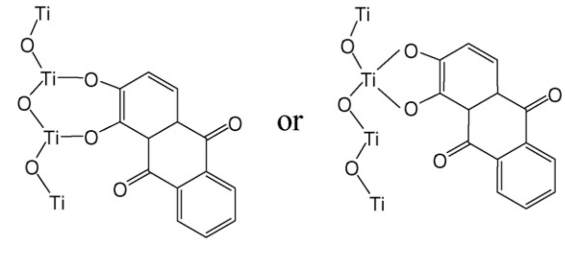
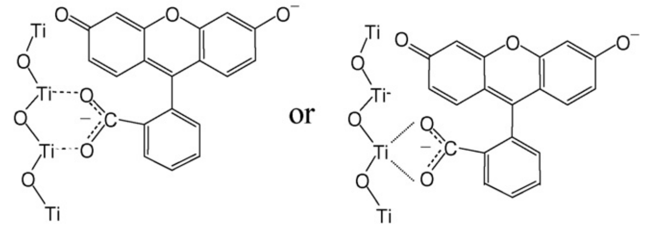


Fig. 5. XRD patterns of the fluorescein- and alizarin-doped titania-gel films steam-treated for 12 h. The fluorescein- and alizarin-doped titania-gel films were prepared from the sol–gel precursor solutions containing 1.0–3.0×10^{-2} mol dm^{-3} fluorescein and 1.0–5.0×10^{-2} mol dm^{-3} alizarin, respectively.



Titania–Alizarin



Titania–Fluorescein

Fig. 6. A schematic interaction model between the dye molecules and titania.

sample are much broader as the dye concentration increased. The results can be interpreted as the dye molecules prevent crystallization of the gel around them. Therefore, the IPCE value did not increase as much as the alizarin concentration. This study suggests that the crystal growth of titania is more important than the interaction between the dye and titania in order to improve the photocurrent in the present systems. In addition to this, the strong interaction also promotes a back electron transfer in the alizarin-adsorbed titania system which results in a low efficiency [27–31]. However, the IPCE values improved with increasing in alizarin concentration in the films because the dye amount was predominant over the crystallinity as shown in Fig. 4b.

The differences in the results between the dyes reflect the difference in the interaction between the dyes and titania. Fig. 6 shows a schematic model of the interaction between the dyes and titania. Alizarin is expected to be strongly bonded by the coordination of Ti on the titania surface to two hydrate groups of the dianion. On the other hand, fluorescein is expected to be bonded in the dianion form by the interaction between its carboxylate group and Ti of the titania surface.

3.4. *Quantum efficiencies of photocurrent generation of electrodes*

The quantum efficiencies of the photocurrent for the excited dye in the electrode samples were estimated as shown in Fig. 7. The values for the fluorescein and alizarin samples were estimated at 500 and 470 nm, respectively, which are the wavelengths of the IPCE maxima for each dye. The efficiency of the fluorescein-doped sample was 0.17% before the steam treatment and increased with the treatment time to 2.3% after the 12-h treatment, whereas that for the alizarin-doped sample was about 1.2% and did not significantly change. The crystallization of titania was found to remarkably improve the efficiency of the photochemical process including the injection from the excited dye to the conduction band-like state of titania. However, the remarkable dye desorption from the fluorescein-doped samples by further steam treatment lowered the quantum efficiency. The IPCE spectrum of the conventional dye-sensitized electrode coincided with its absorption spectrum. Both the IPCE and quantum efficiency at 500 nm were 0.63% because the thick film of the electrode absorbed almost all of the photons from the light source. Compared with the conventional sample, the IPCE of the 12-h treated fluorescein sample is lower, but its quantum efficiency is much higher. The IPCE values and the quantum efficiency of the photocurrent in the fluorescein-doped electrodes are not much higher than in the other studies of the dye-sensitized solar cells. However, the present study suggests the ability to improve the photocurrent efficiency under certain conditions. The moderate interaction between the dye and titania and the high crystallinity allow the absorbed light energy to be effectively utilized.

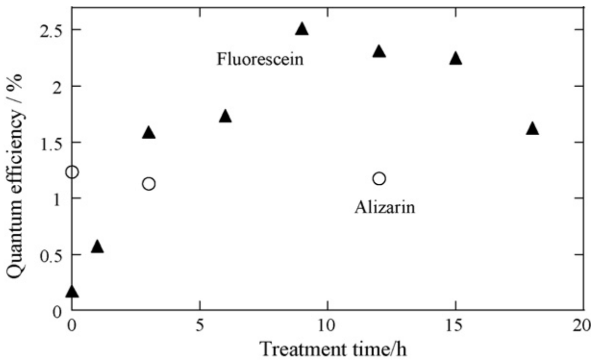


Fig. 7. Changes in quantum efficiencies of photocurrent in the fluorescein- and alizarin-doped titania-gel films due to the steam treatment.

4. Conclusions

A photocurrent was observed in the fluorescein- or alizarin-doped titania-gel film during visible light irradiation, resulting from the electron transfer from the excited state of the dye to the conduction band-like states of the titania gel. An anatase-type crystal was produced by the steam treatment of the titania gel. The IPCE value and the quantum efficiency of the photocurrent in the fluorescein-doped electrode remarkably improved with the duration of the steam treatment because the crystallization of the titania gel increased its electric conductivity. The quantum efficiency increased by 14 times after the 12-h steam treatment. On the other hand, the photocurrent hardly changed and the crystal slightly grew by the steam treatment of the alizarin-doped films. Alizarin molecules prevented the crystal growth of the titania gel due to the strong interaction with the Ti around them.

Acknowledgments

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