Influence of adding carbon nanotubes on photoelectric conversion properties of dye-doped titania gel

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Abstract

Multiwalled carbon nanotubes (MWCNTs) were incorporated into amorphous dye-doped titania gel by the sol-gel method at room temperature. The working electrodes were prepared by coating the ITO glass with the sol-gel titania precursor containing the dye and MWCNTs. The photoelectric conversion properties of the electrodes were examined by simple spectroscopic and electric measurements. The photocurrent spectrum originated from the absorption of the dye. The short circuit photocurrent was enhanced by adding a small amount of MWCNTs evenly to the amorphous dye-doped titania gel. The open circuit voltage was due to the semiconducting characteristics property of the titania gel. The experimental results indicated the electron transport from the dye excited states to the MWCNTs through the titania gel. The MWCNTs functioned as bridges between the titania and ITO. Steam treatment of the titania gel electrodes significantly increased the photoelectric performance due to crystallization of the titania and enhancement of the dye-titania interaction forming the chelate complex on the titania particle surface.

Introduction

Ultimate photoelectric conversion materials, nano-sized solar cells or photosensors, allow the development of high quality electronic devices containing nanoscale circuits. Many scientists have studied dye-sensitized solar cells based on titania nanoparticles as new energy generators or photoelectronic devices [1−3]. Carbon nanotubes (CNTs) have quantum characteristics and are promising for applications in novel electronic devices [4−8]. The composition of these materials with titania provides effective characteristics for electronic technology such as photocatalysts or dye-sensitized solar cells [9−15]. Low temperature processes may be required in order to use heat-resistless materials. We previously investigated the photo-induced electron transfer and photocurrent in dye-doped titania gel, i.e., unheated titania gels containing a dispersed dye [16−20]. The dye-doped gel films are prepared without heating from a titanium alkoxide sol containing the dye molecules by the sol−gel method. The characteristics of the dye-doped titania system include a high dispersion of the dye and a high contact area between the dye and titania. The gel consists of amorphous, nanosized, and particle-like units, which have a semiconductor-like quasi-conduction band structure with a low density of states [16−18]. The dye molecules exist in the nanopores of the gel. The dye-doped titania gel is an interesting material for the basic study of dye-sensitized solar cells because hydrothermal treatments cause its crystallization and the changes in the titania structure and the dye-titania bond character.

A nanocomposite consisting of such an amorphous dye-doped titania gel and multiwalled carbon nanotubes (MWCNTs) was then prepared by a simple low-temperature process, and its photoelectric properties were measured by simple techniques [21,22]. This material has a structure in which the thin film of the MWCNT bundles was coated with the dye-doped titania gel film. Furthermore, the dye- and titania gel-modified MWCNT nanoelectrodes were prepared by the sol-gel method at room temperature [23]. The individual MWCNTs were combined with the dye-modified titania gel in order to prepare the nanoelectrode in which the dye-titania gel-MWCNTs are chemically bonded.

The photocurrent spectrum originated from absorption of the dye.   The open-circuit voltage was due to the semiconducting characteristics of the titania gel involving a certain conduction band level. The experimental results indicated electron transport from the dye excited states to the MWCNTs through the titania gel.   Such nanoelectrodes were valid for the photoelectric conversion because the MWCNTs functioned as the bridge between the titania particles and ITO electrode.   However, more simple nanocomposite electrodes are required for easier preparation.

We have investigated the interaction between the dye and the titania in the fluorescein-doped titania and its photoelectric conversion properties [16–23].   The quantum efficiency of the electron injection from the dye to the titania gel was improved by the steam treatment due to the dye-titania complex formation.   Fluorescein is, therefore, useful for the basic systematic study of dye-titania systems. In this study, MWCNTs were incorporated to a fluorescein dye-doped titania gel by the sol-gel method at room temperature.   The action electrodes were prepared by coating the ITO glass with the sol-gel titania precursor containing the dye and MWCNTs.   The photoelectric conversion properties of the electrodes were examined by simple spectroscopic and electric measurements in order to clarify the influence of adding MWCNTs on the photoelectric conversion properties of the dye-doped titania gel electrodes.   Furthermore, we also investigated the influence of steam treatment of the titania gel electrodes on their photoelectric conversion properties.   The reduced MWCNTs are produced as intermediate species in the role of the bridge between the titania particles and ITO electrode.   These intermediate species should be quickly oxidized by donating the electrons to the ITO electrode. These processes are important for high performance of the dye-doped titania gel electrodes.   The electron transport from the dye to the ITO electrode through the titania gel and the MWCNTs was examined compared to the back electron transfer from the titania gel or the ITO to the electrolyte.

Experimental section

Materials

Titanium tetraisopropoxide, ethanol, fluorescein, hydrochloric acid, sulfuric acid, nitric acid, diethylene glycol, iodine, and lithium iodide (S or reagent grade; Wako Pure Chemicals), were used without further purification.   Water was ion-exchanged and distilled.   Glass plates coated with the ITO transparent electrode (AGC Fabritech) were soaked in hydrochloric acid (1.0 mol dm^{-3}) for 2 h and then rinsed with water.   The electrolyte used for the electrical measurements consisted of an diethylene glycol solution of iodine (5.0×10^2 mol dm^{-3}) and lithium iodide (0.50 mol dm^{-3}).

The MWCNTs (95% purity; Ilijin Nanotech) have a diameter of 10–30 nm and a length of 10–20 μm. In order to increase their dispersibility into matrices and reactivity with the titania precursor, the MWCNTs were treated with a concentrated H_2SO_4/HNO_3 mixture (3/1 in volume) at 313K for 48 h and then rinsed with a copious amount of water [21,23−26].   The acid-treated MWCNT sample was dried at 393 K and labeled as ACNT.

Preparation of electrodes

The suspensions A were prepared by mixing 10.0 cm^3 of titanium tetraisopropoxide, 0−20.0 mg of ACNT, and 0−100 mg of fluorescein.   The suspensions B were prepared by mixing 25.0 cm^3 of ethanol, 0.21 cm^3 of water, and 0.21 cm^3 of nitric acid (60 wt%) as the catalyst for the sol–gel reaction. Titania, 2.68 g, can be ideally obtained from 10.0 cm^3 of titanium tetraisopropoxide.   The amounts of the ACNT and fluorescein were much smaller than that of the titania.   The sol-gel reaction systems were prepared by mixing suspensions A and B and stirring for 10 min.   Three layers of the dip-coated thin films were made on the ITO electrodes from the sol–gel systems reacting for 1 day in order to prepare the electrodes in this study.   The ITO electrodes were withdrawn from the sols at 160 μm s^{-1}.   This led to the obtaining of the ACNT-dispersing dye-doped titania gel electrodes. These working electrodes were treated with steam in order to investigate the steam-treatment effects on the UV-visible absorption and photocurrent spectra of the electrode samples.   Water was heated at 383 K, and the electrode samples were exposed to its steam for 120 min.   The pressure of the steam was about 140 kPa.

Measurements

The surface morphology of the electrode samples was observed and their layer thickness was estimated from their cross section using a field emission scanning electron microscope (Hitachi S-4100).   The thickness of the titania gel layers was ca. 210 nm which slightly changed by the steam treatment.   The UV−vis absorption spectra of the prepared electrode samples were observed in the transmission mode using a spectrophotometer (Shimadzu UV-3150).   The iodine-based electrolyte was allowed to soak into the space between the electrode sample and the counter Pt electrode. Monochromatic lights obtained from a fluorescence spectrophotometer (Shimazdu RF-5300) with a 150-W Xe short arc lamp (Ushio UXL-155) were irradiated on the electrodes for the spectroscopic measurements. Under light irradiation, the short circuit currents of the electrodes were measured by an electrometer (Keithley model 617).   The I−V curves of the electrodes were measured by a potentiostat (Hokuto Denko HSV-100) during irradiation by visible light with a wavelength longer than 400 nm emitted by the 150-W Xe short arc lamp using a sharp cut-off filter.   The intensity at each wavelength of the light source was obtained using a power meter (Molectron PM500A) in order to estimate the quantum efficiency for the photocurrent from the excited dye in the electrode samples. The light intensity was confirmed to correlate with the results of the potassium ferrioxalate actinometry. The visible absorbance of the present electrode samples was lower than 1.0, which was sufficient to measure the number of absorbed photons in order to calculate the quantum efficiency.

Results and discussion

Dependence of photoelectric conversion properties on ACNT amount

Figure 1 shows the SEM images of the surface and cross section of the untreated titania gel electrodes prepared from the sols containing 5.0, 10.0, and 20.0 mg of ACNT, which was dispersed in the whole titania gel and also distributed on the surface without forming its large aggregates.   No

tubes were observed on the surface of the electrodes containing a CNT amount smaller than 10.0 mg because most of the ACNT was incorporated in the titania gel.

(Fig. 1)

The UV-vis absorption spectra of the untreated titania gel electrodes prepared from the sols containing 5.0 mg of fluorescein and 0−20.0 mg of ACNT exhibited a slight absorption originating from the fluorescein and ACNT due to their low amounts (supporting information, Fig. S1).   The electrode prepared from the sol containing 0 mg of ACNT indicates the dye-doped titania gel electrode without ACNT.   The absorption spectra contained only the UV absorption and interference patterns due to the titania gel films.   Figure 2 shows the photocurrent spectra of the above titania gel electrodes.   The photocurrent density values in the UV and visible ranges were due to the titania gel and dye absorptions, respectively.   These values increased and then decreased with an increase in the ACNT amount.   The increase is because the ACNT enhanced the electron transport from the titania to the ITO electrode.   The ACNT functioned as the bridges between the titania particles and ITO electrode as previously reported [21−23].   However, as a higher amount of the ACNT was dispersed in the titania gel, they were also in contact with the electrolyte.   This is expected due to the SEM images of the electrode surface shown in Fig. 1.   This induced the back electron transfer from the titania gel to the electrolyte and charge recombination causing a decrease in the photocurrent.   Figure 3 shows the $I-V$ curves of the above titania electrodes during visible light irradiation.   The short circuit current density values varied with the ACNT amount corresponding to those in the photocurrent spectra.   The open circuit voltage values for these electrodes were not significantly different, 0.22−0.23 V, which were due to the semiconducting characteristics property of the titania gel involving a certain conduction band level [21−23].   The short circuit between the electrolyte and the ITO electrode through ACNT can decrease the open circuit voltage values.   However, the experimental results indicated that the ACNT caused the electrical contact between the titania gel and the electrolyte but did not cause the short circuit between the electrolyte and the ITO electrode.

(Figs. 2 and 3)

Dependence of photoelectric conversion properties on dye amount

Figure 4 shows the visible absorption spectra of the untreated titania gel electrodes prepared from the sols containing 0−100 mg of fluorescein with 5.0 mg of ACNT compared to that of fluorescein in water. The absorption spectra contained interference patterns depending on the film thickness. The absorption due to the dye clearly appeared in the electrodes containing a dye amount greater than 10.0 mg. The spectral bands for these electrodes were observed around 400−550 nm. Their peaks at 490−500 nm are assigned to the mixture of the anion and dianion species of fluorescein, based on the spectra observed in water [27]. In addition, the longer wavelength band indicates the formation of the dianion-like species resulting from the strong interaction and a chelating linkage between the carboxyl group of the dye and the titanium species [16−20]. The absorption due to ACNT was not clearly observed because its amount was much smaller than that of the titania gel.

(Fig. 4)

Figure 5 shows the photocurrent spectra of the above titania electrodes. The photocurrent density values decreased with an increase in the dye amount in the UV range whereas they increased in visible range. The higher amount of the dye molecules caused the decrease in the titania conductivity due to the insulating characteristics of the dye. The photocurrent values in the UV range for the electrode containing 50.0 mg of fluorescein were about half of those for the electrode containing 5.0 mg of fluorescein. On the other hand, the photocurrent values in the visible range for the former were about three times higher than those for the latter. The photocurrent in the visible range was enhanced by the sensitization effect of ten times increase in the dye amount. This effect was greater than that of the decrease in the titania conductivity. Figure 6 shows the $I-V$ curves of the above titania electrodes during the visible light irradiation. The short circuit current density values varied with the dye amount corresponding to those of the photocurrent spectra in the visible range. The

open circuit voltage values increased with a decrease in the electrode conductivity due to the insulating characteristics of the dye.

　(Figs. 5 and 6)

Effect of steam treatment

　Figures 7 and 8 show the photocurrent spectra and the I−V curves observed during visible light irradiation, respectively, for the steam-treated titania electrodes containing 100 mg of fluorescein with 0−10.0 mg of ACNT.　 The photoelectric conversion properties of the untreated and steam-treated electrodes are summarized in Table 1.　 The crystallization to anatase-type titania under this condition was confirmed in our previous study [16−20].　 The photocurrent values significantly improved by the steam treatment due to crystallization of the titania and enhancement of the dye-titania interaction as previously reported [19,20].　 The open circuit voltage values also increased similarly to those previously observed in the steam-treated titania electrodes due to enhancement of the dye-titania interaction [19,20].　 The values of the maximum power and quantum efficiency for photoelectric conversion were also significantly improved.　 The maximum values of the photoelectric conversion properties were observed in the electrode containing 5.0 mg of ACNT as well as in the untreated electrode.　 The ACNT also functioned as the bridges between the titania particles and ITO electrode in the steam-treated electrodes.　 It is important that the ACNT improved the electrical contact between the titania and ITO electrode but did not cause the contact between the titania and electrolyte.

　(Figs. 7 and 8 and Table 1)

　As shown in Figs. 4 and 5, peaks in the visible absorption and photocurrent spectra of the untreated electrodes were located around 400−550 nm, ranging over a wavelength wider than that observed in various solvents.　 This result indicated that the main fluorescein species were the dianion form [27] and were in the titania gel phase.　 Fluorescein molecules should be in the neutral or cation form if they are adsorbed on the ACNT surface, which has neutral characteristics on the graphene sheet and proton-accepting characteristics on the oxidized groups [24−26,28,29].　 In addition, the longer

9

wavelength band indicated that a low number of fluorescein molecules formed the dianion-like species resulting from the strong interaction and a chelating linkage between the carboxylate group of the dye and the titanium species [30−36]. The absorbance decreased to one-third, and the spectral shape became broader to the longer wavelength side due to the steam treatment [16−20,35]. These results indicated that the species weakly trapped in the pores of the gel were preferentially desorbed from the inside of the titania gel film into the water phase. The steam treatment probably increased the number of fluorescein molecules interacting with the titanium species. The chelate complex formed on the titania particle surface plays an important role in the photoelectric conversion.

The photocurrent values of the steam-treated electrodes were still low compared to the general dye-sensitized solar cells because the crystallinity and electric conductivity of the steam-treated titania were lower than those of crystalline titania prepared by heating [16−20]. A steam treatment at higher temperature and pressure can further improve the photoelectric conversion performance.

Conclusions

ACNT was incorporated into the fluorescein-doped titania gel by the sol-gel method at room temperature. The photoelectric conversion properties of the dye-doped titania electrodes containing ACNT were examined by simple spectroscopic and electric measurements. The photocurrent density values in the UV and visible ranges were due to the titania gel and dye absorptions, respectively. These values increased and then decreased with an increase in the ACNT amount. The increase is because the ACNT enhanced the electron transport from the titania to the ITO electrode. The ACNT functioned as bridges between the titania particles and ITO electrode. However, as a higher amount of the ACNT was dispersed into the titania gel, they also easily came into contact with the electrolyte. This induced the back electron transfer and charge recombination, causing a decrease in the photocurrent. The open circuit voltage was due to the semiconducting characteristics property of the titania gel. The photocurrent density values decreased with an increase in the dye amount in the UV

range whereas they increased in the visible range.   The higher amount of the dye molecules caused the decrease in the titania conductivity due to the insulating characteristics of the dye.   The photocurrent in the visible range was enhanced by the sensitization effect of the dye amount.   This effect was greater than that of the decrease in the titania conductivity.   Steam treatment of the titania gel electrodes significantly increased the photoelectric performance due to crystallization of the titania and enhancement of the dye-titania interaction forming the chelate complex on the titania particle surface.

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Table 1. Photoelectric conversion properties of the untreated and steam-treated electrodes prepared from the titanium alkoxide sol containing 100 mg of fluorescein and 0−10.0 mg of ACNT.

ACNT amount / mg	I_{SC} / μA cm^{-2}	V_{OC} / V	FF	P_{max} / μW cm^{-2}	QE / %
Untreated					
0	0.45	0.26	0.33	0.039	0.0034
5.0	0.95	0.29	0.36	0.10	0.0070
10.0	0.40	0.23	0.30	0.028	0.0029
Steam-treated					
0	19	0.31	0.48	2.8	0.45
5.0	43	0.37	0.60	9.5	1.1
10.0	29	0.34	0.56	5.5	0.64

I_{SC} : short circuit photocurrent density
V_{OC} : open circuit voltage
FF : fill factor
P_{max} : maximum power
QE : quantum efficiency at 500 nm

Figure captions

Figure 1   SEM images of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing 5.0 mg of fluorescein and (a, b) 5.0, (c, d) 10.0, and (e, f) 20.0 mg of ACNT

Figure 2   (a) UV and (b) visible photocurrent spectra of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing 5.0 mg of fluorescein and (1) 0, (2) 1.0, (3) 5.0, (4) 10.0, and (5) 20.0 mg of ACNT
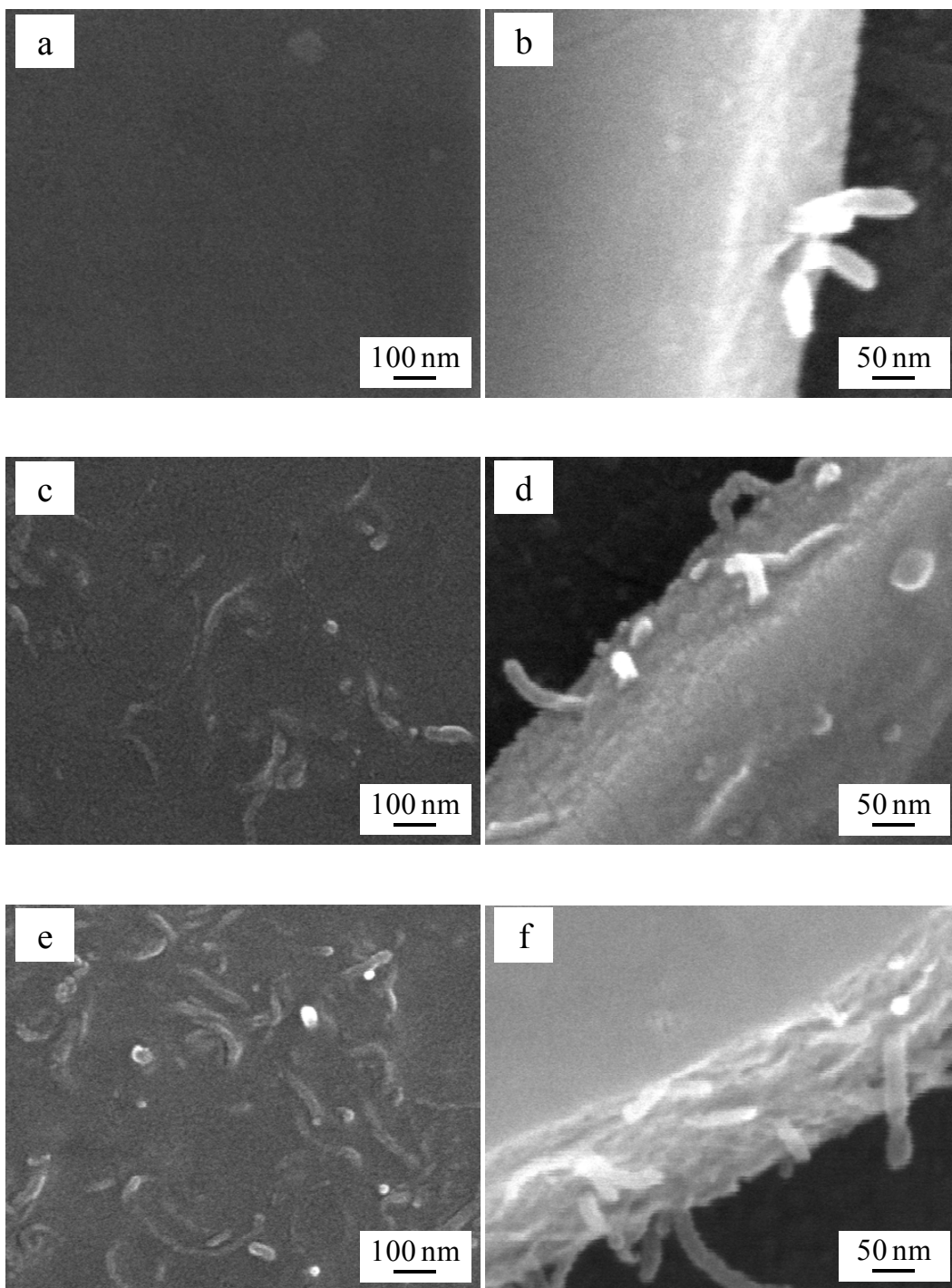
Figure 3 $I-V$ curves of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing 5.0 mg of fluorescein and (1) 0, (2) 1.0, (3) 5.0, (4) 10.0, and (5) 20.0 mg of ACNT

Figure 4   Visible absorption spectra of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing (1) 0, (2) 10.0, (3) 50.0, and (4) 100 mg of fluorescein and 5.0 mg of ACNT and visible absorption spectrum of (5) fluorescein in water

Figure 5   (a) UV and (b) visible photocurrent spectra of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing (1) 0, (2) 5.0, (3) 10.0, (4) 50.0, and (5) 100 mg of fluorescein and 5.0 mg of ACNT

Figure 6   *I−V* curves of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing (1) 0, (2) 5.0, (3) 10.0, (4) 50.0, and (5) 100 mg of fluorescein and 5.0 mg of ACNT

Figure 7   (a) UV and (b) visible photocurrent spectra of the steam-treated titania electrodes prepared from the titanium alkoxide sol containing 100 mg of fluorescein and (1) 0, (2) 5.0, and (3) 10.0 mg of ACNT
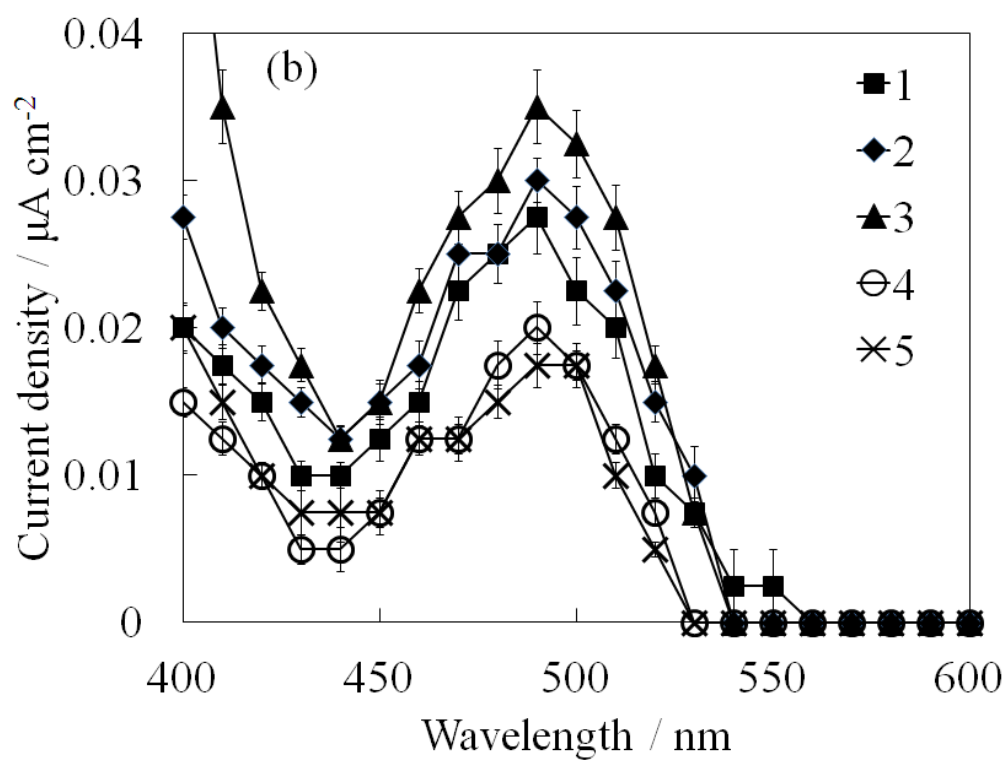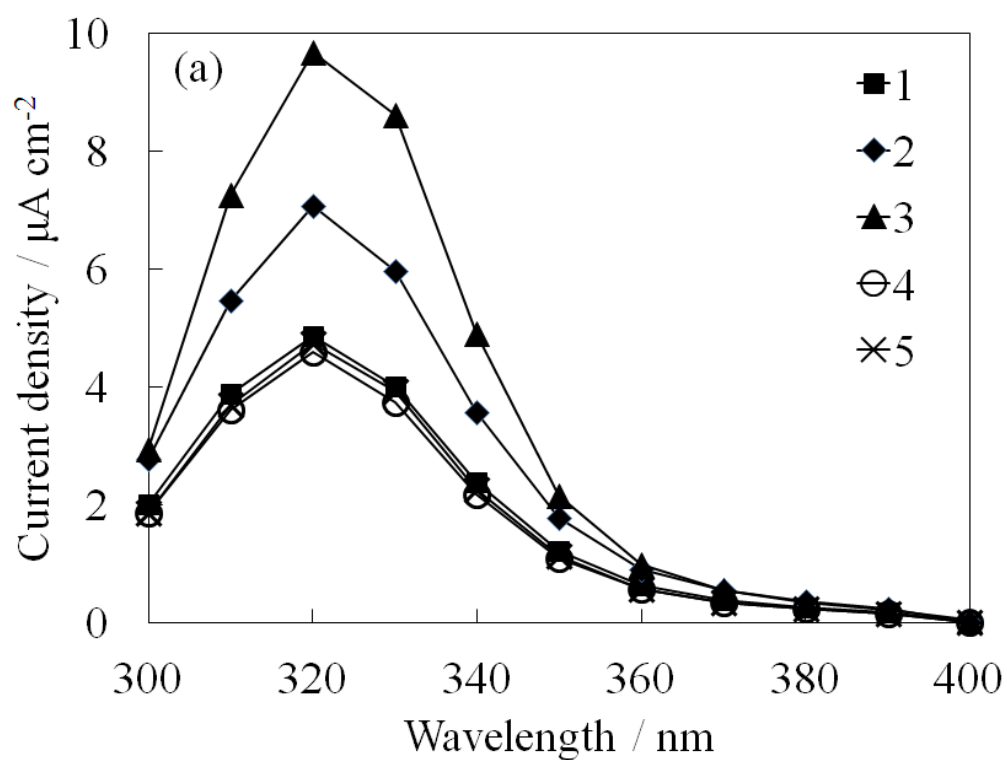
Figure 8   *I−V* curves of the steam-treated titania electrodes prepared from the titanium alkoxide sol containing 100 mg of fluorescein and (1) 0, (2) 5.0, and (3) 10.0 mg of ACNT

Figure 1

Figure 2

Figure 3
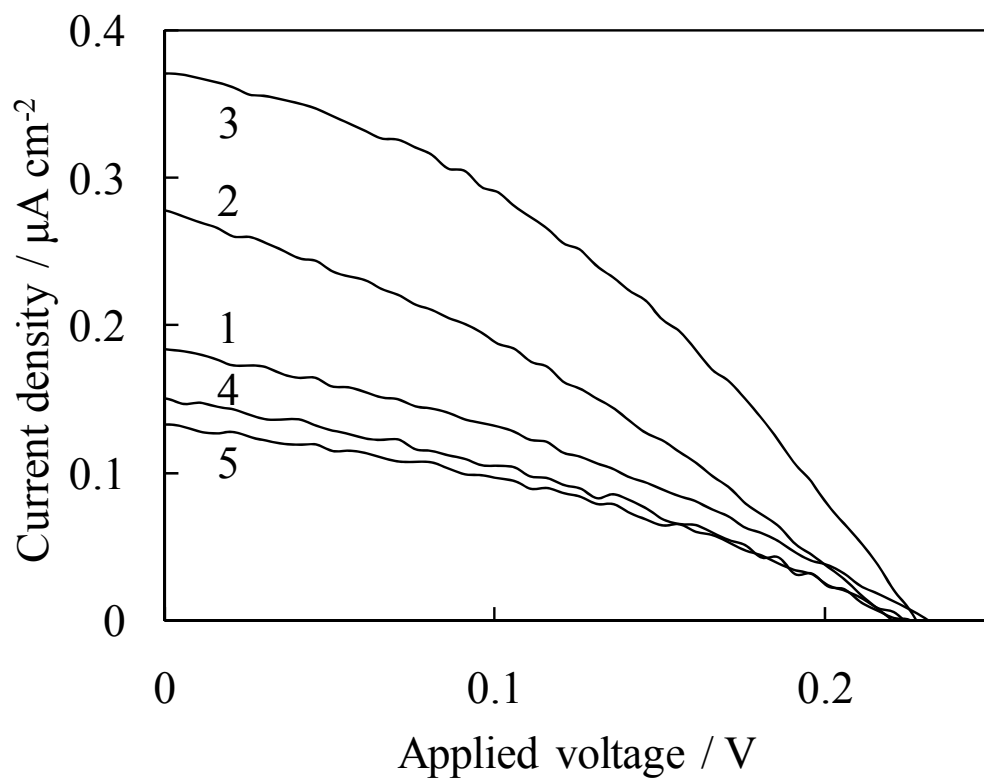
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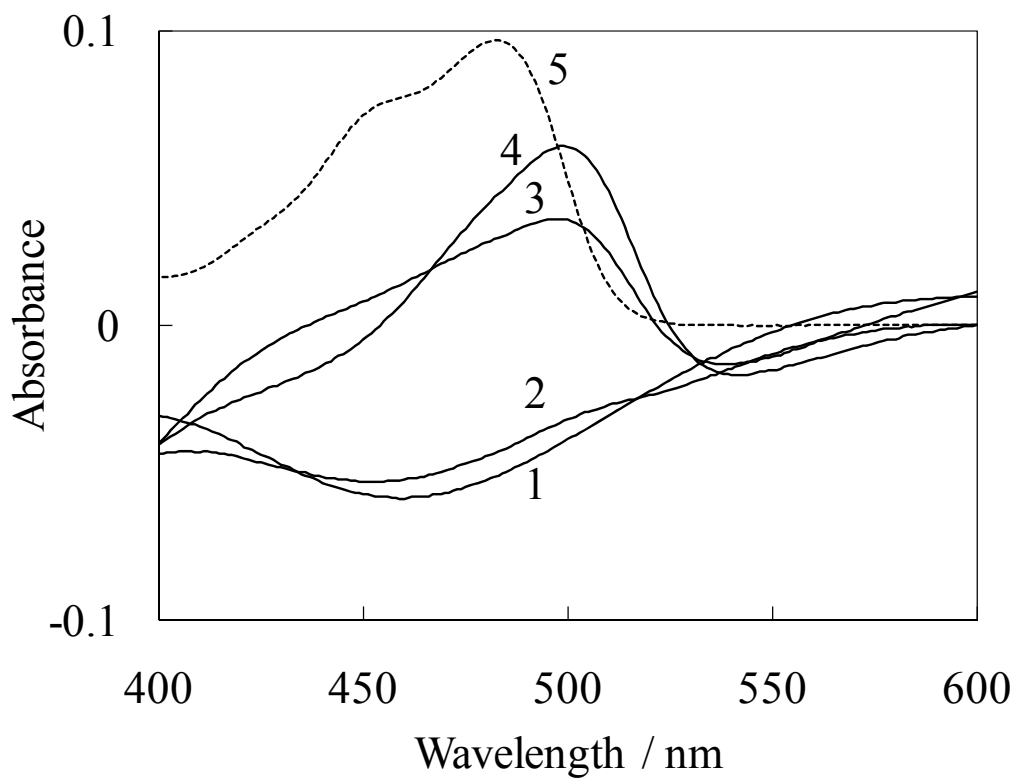
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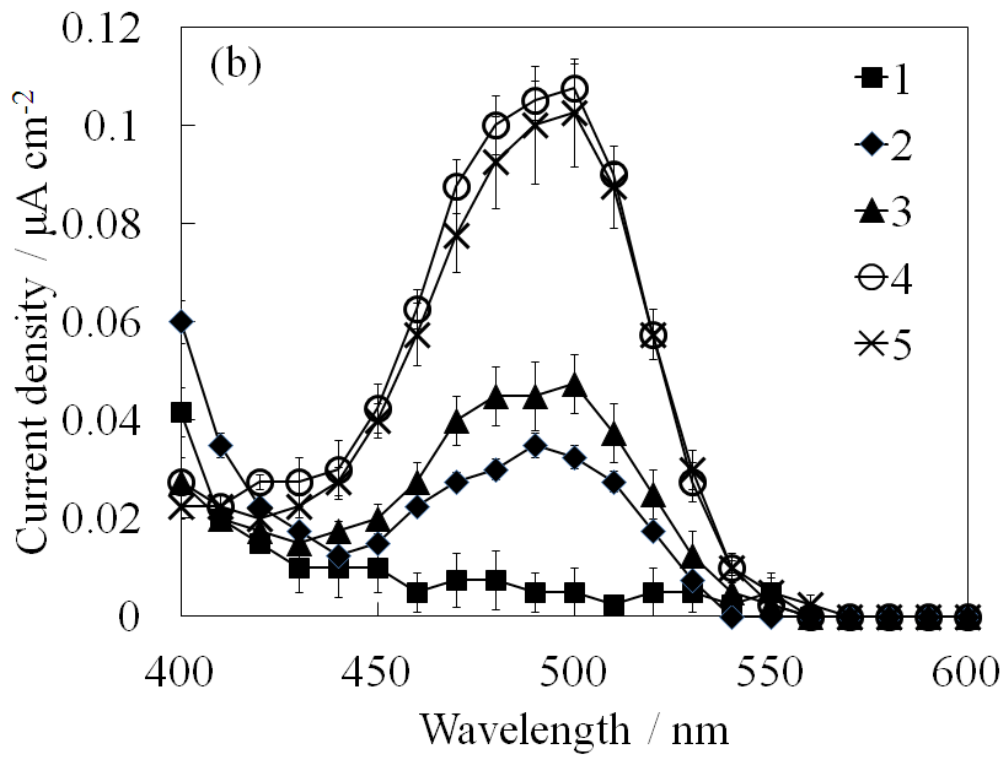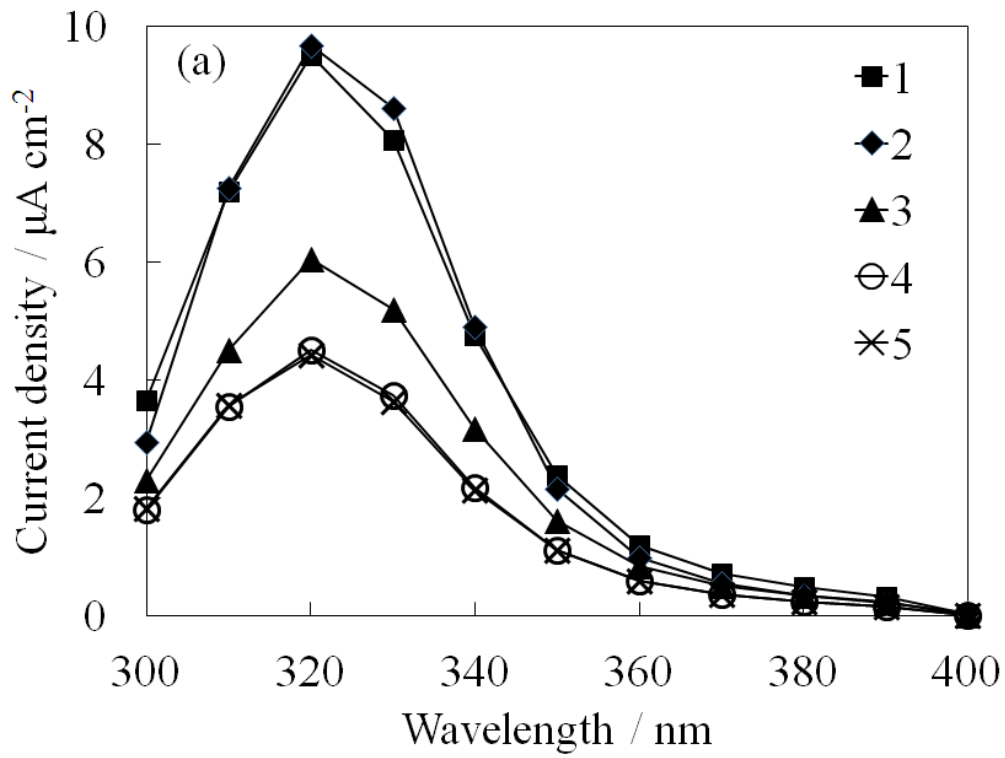
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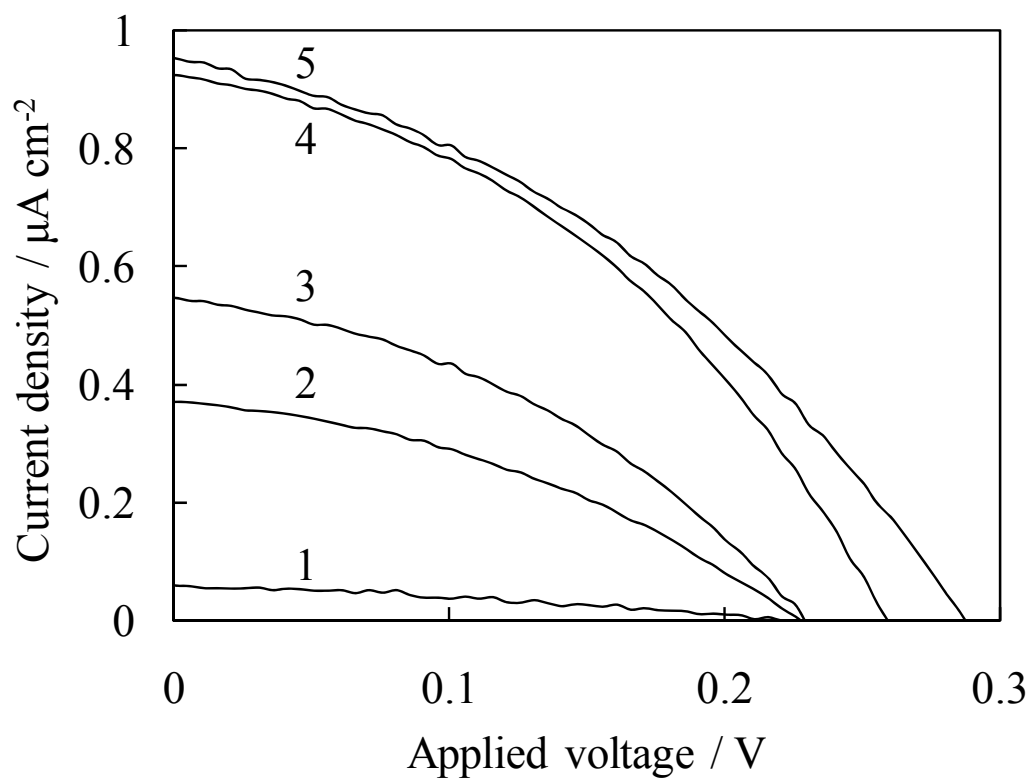
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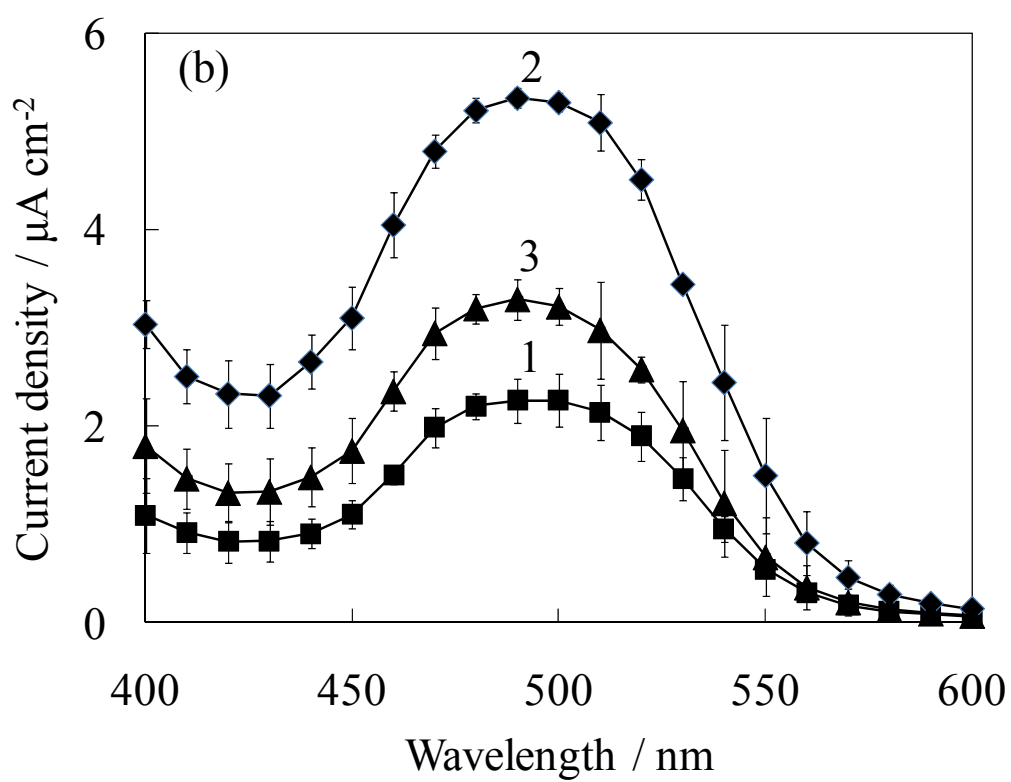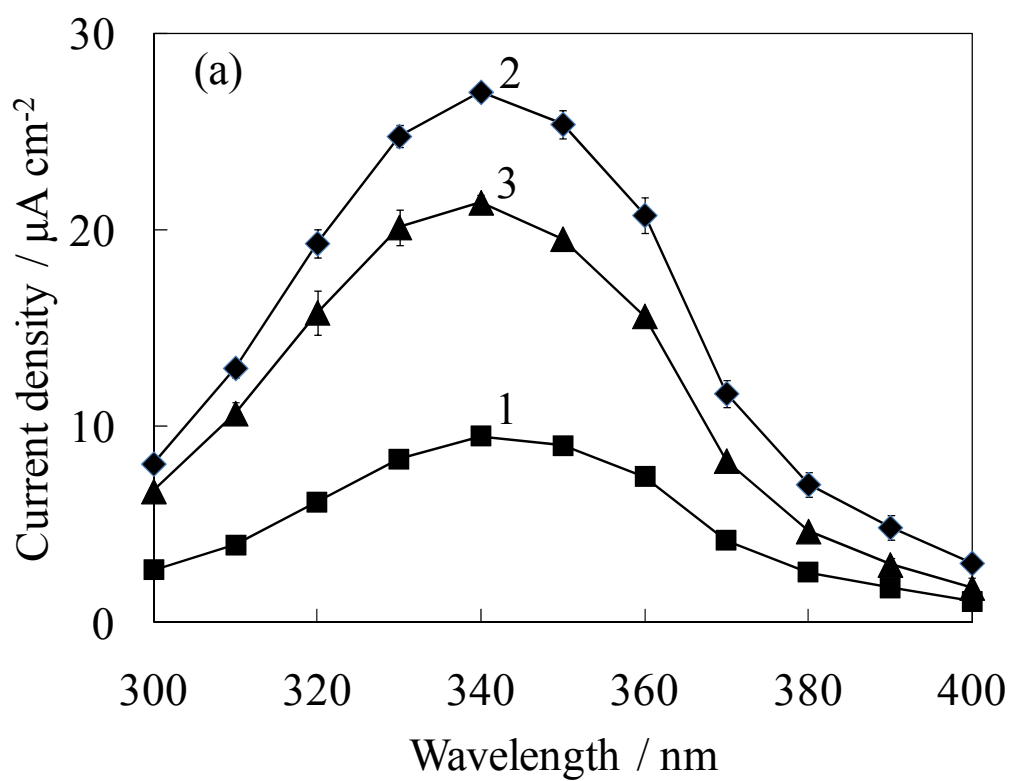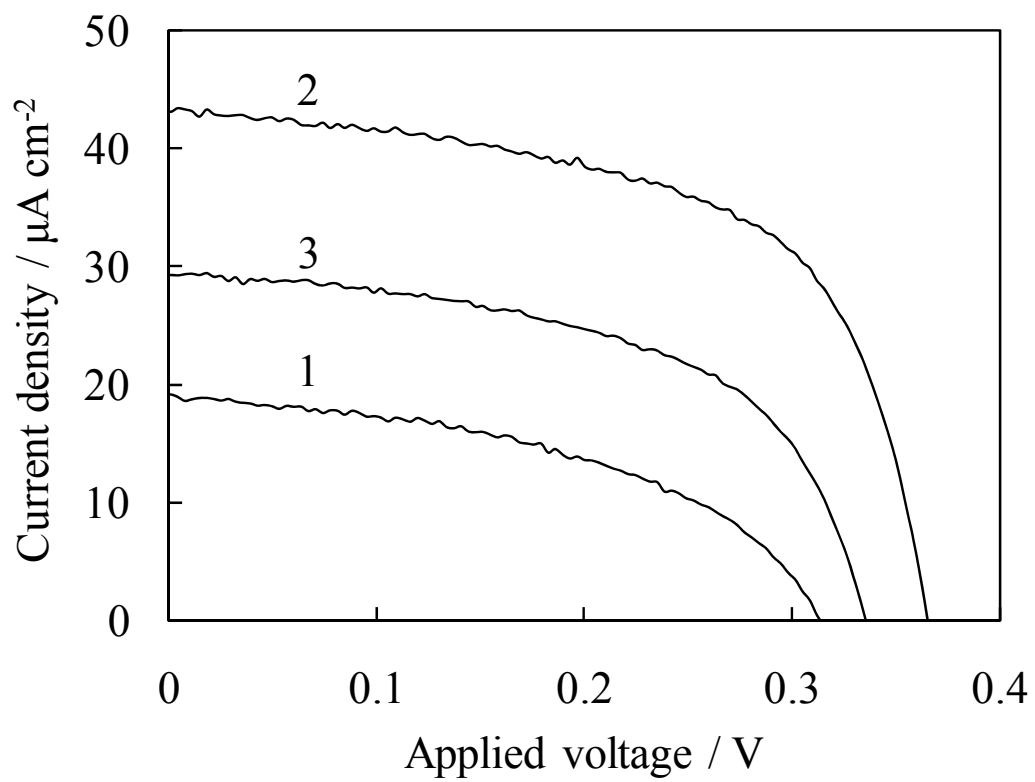
Figure 8

Figure S1 UV-vis absorption spectra of the untreated titania gel electrodes prepared from the titanium alkoxide sols containing 5.0 mg of fluorescein (1) without and (2) with 20.0 mg of ACNT