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Photocurrent Generated from Nanoelectrode Consisting of Dye, Titania Gel, and Carbon Nanotube

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The dye- and titania gel-modified multiwalled carbon nanotube nanoelectrodes were prepared by sol–gel at room temperature. The photoelectric conversion properties of the nanoelectrodes were examined by simple spectroscopic and electric measurements. The photocurrent spectrum originated from the absorption of the dye. The open-circuit voltage was due to the semiconducting characteristics of the titania gel. The experimental results indicated electron transport from the dye excited states to the carbon nanotubes through the titania gel.

Nanosized solar cells or photosensors allow the development of high-quality electronic devices containing nanoscale circuits. Dye-sensitized solar cells based on titania nanoparticles have received significant attention as new energy generators and photoelectronic devices.[1] Carbon nanotubes (CNTs) have quantum characteristics and are promising for applications in novel electronic devices.[2,3] The composition of these materials provides effective characteristics for electronic technology.[4–8] We previously investigated the photoinduced electron transfer and photocurrent in unheated titania gels containing a dispersed dye.[9] Furthermore, a nanocomposite consisting of such dye-doped titania gel and multiwalled carbon nanotubes (MWCNTs) was prepared by a simple low-temperature process, and its photoelectric properties were measured by simple techniques.[10] However, this material has a structure in which the thin film of the MWCNT bundles was coated with the dye-doped titania gel film. In this study, the individual MWCNTs have been combined with the dye-modified titania gel in order to prepare nanoelectrodes in which the dye–titania gel–MWCNTs are chemically bonded.

The materials used in this study, the acid treatment procedures of the MWCNTs, and electrochemical measurements have been previously described.[10,11] The acid-treated MWCNT is referred to as ACNT.

Fluorescein dye (FC), 10.0 mg, and ACNT, 100 mg, were dispersed in titanium tetraisopropoxide (TTIP), 20.0 cm^3, by ultrasonic irradiation for 1 h in order that the TTIP forms polymer, amorphous titania gel (TG), and bonds to the FC and ACNT. This suspension was vacuum filtered using a 0.1-µm pore size membrane filter in order to remove the unreacted FC and TTIP. The resulting precipitate was rinsed with ethanol and dried at 373 K. This sample was labeled FC–TG–ACNT. Also, a sample without FC, TG–ACNT, and a sample without ACNT, FC–TG, were prepared.

These samples were dispersed in *N*,*N*-dimethylformamide by ultrasonic irradiation for 1 h. These suspensions were deposited onto ITO–glass plates and dried at 373 K to prepare the electrodes containing each sample. TTIP was also deposited onto an ITO–glass plate to form the electrode, TG.

The surface of the electrode samples was observed using a transmission electron microscope (JEOL JEM-2010). Flakes of the film samples were pressed in KBr pellets, and their IR spectra were taken using an FTIR spectrophotometer (Shimadzu FTIR-8300). The UV–vis absorption spectra of the prepared electrode samples were observed in transmission using a spectrophotometer (Shimadzu UV-3150).

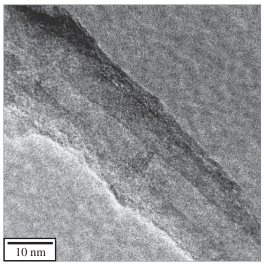

Figure 1. TEM image of the FC–TG–ACNT composite.

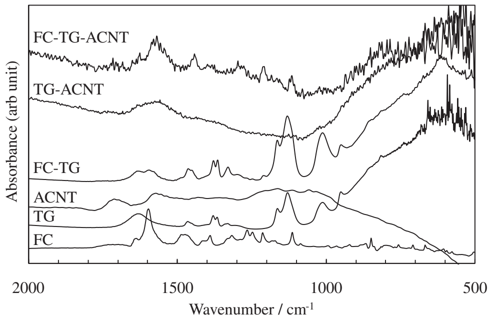

Figure 2. FTIR spectra for each sample.

Figure 1 shows a TEM image of the FC–TG–ACNT sample. One of the CNTs is covered with a specific thin amorphous TG film.

Figure 2 shows the FTIR spectra for each sample. In FC, carboxy C=O stretching vibration and carboxylate COO^- antisymmetric and symmetric stretching vibrations were observed at 1710, 1597, and 1390 cm^{-1}, respectively. In addition, the band at around 1460 cm^{-1} was assigned to the quinone-like C=O stretching vibration.[12] TG shows a peak at 1640 cm^{-1} assigned to the O–H bending vibration of the adsorbed water and a peak at around 600 cm^{-1} assigned to the Ti–O stretching vibration of the TG.[9a] The peaks at 1400–900 cm^{-1} were assigned to the incompletely reacted TTIP.[11a] ACNT shows peaks at 1713 (C=O stretching), 1580 (C=C stretching), and 1200–1000 cm^{-1} (O–H bending and C–O–C stretching). In the FC–TG spectrum, no C=O peak was observed and the carboxylate COO^- antisymmetric and quinone-like peaks were located at 1590 and 1450 cm^{-1}, respectively, lower than their peak wavenumbers for FC.[12] This indicates the complex formation of FC and Ti of TG. TG–ACNT shows no C=O band and two new

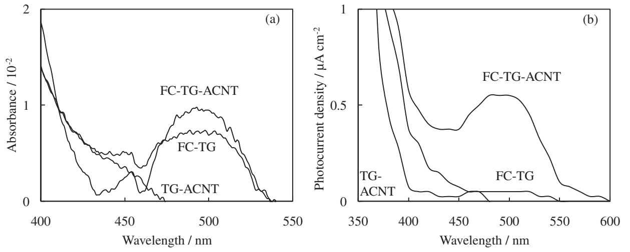

Figure 3. (a) UV–vis absorption and (b) photocurrent spectra of each sample.

broad bands at around 1500 and 1400 cm^{-1} assigned to the COO$^-$ antisymmetry and symmetry stretching vibrations, respectively.[11a] In addition, the spectrum indicates that the incompletely reacted TTIP further reacted, growing the O–Ti–O networks. The spectrum of FC–TG–ACNT shows peaks at 1688, 1568, 1480, 1433, and around 600 cm^{-1}, indicating the formation of chemical bonding between the FC and TG and the TG and ACNT.

Figure 3 shows a comparison of the UV–vis absorption and photocurrent spectra of each sample. The spectral bands for FC–TG–ACNT and FC–TG were observed around 400–550 nm due to the absorption of FC. The photocurrent values are 10-fold enhanced by the presence of the ACNT. Their peaks at 490–500 nm are assigned to the mixture of the anion and dianion species of FC, based on the spectra observed in water.[9,13] 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 carboxy group of the dye and the titanium species.[9] The correspondence between the absorption and photocurrent spectra indicates that the electrons were produced by light absorption of FC and electron transfer from its excited states to the TG.[9,10] The enhanced photocurrent is not due to the CNT absorption because only a weak photocurrent was observed in the ACNT–TG. It is noted that a photocurrent should be generated even in the unheated dye-doped TG as reported in a previous paper.[9] The electron transfer efficiently occurs because the dye molecules are highly dispersed into the TG network on a molecular level. The individual CNTs are coated with the dye-doped TG layer in the composite, and the electron is easily injected into the ITO electrode via the CNTs due to the excellent bridge and interconnection between the TG and the ITO electrode.[4–8,10]

Figure 4 shows the *I*–*V* curves of FC–TG–ACNT and FC–TG observed during visible light irradiation. The short-circuit photocurrent density value of FC–TG–ACNT, 170 µA cm^{-2}, is remarkably higher than that of FC–TG, 1.2 µA cm^{-2} relating to their photocurrent spectra shown in Figure 3. The open-circuit voltage of FC–TG–ACNT, 0.16 V, however, is lower than that of FC–TG, 0.21 V. This is due to the charge recombination at the interface between the TG and the CNTs.[4a] The short circuit between the CNTs and the electrolyte also causes a decrease in the V_{OC} value. The maximum power values for FC–TG–ACNT and FC–TG were 7.7 and 0.11 µW cm^{-2}, respectively. The fill factor for FC–TG–ACNT, 0.28, was lower than that for FC–TG, 0.42, because the ACNT partially inserted between the TG and the ITO decreased its parallel resistance. The quantum efficiencies of the photoelectric conversion for FC–TG–ACNT and FC–TG were 0.29 and 0.026%, respectively. The enhancement of the photocurrent due to the presence of the CNTs improved these values. Even though these values are very low for use in a solar cell, a further improvement is expected after crystallization of the TG by treatment at low temperature, such as steam treatment.[9]

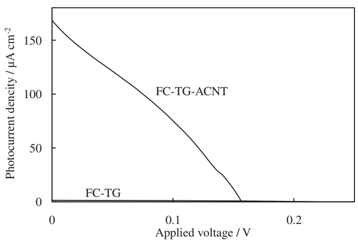

Figure 4. *I*–*V* curves of FC–TG–ACNT and FC–TG observed during visible light irradiation.

In conclusion, a photocurrent was observed in a nanoelectrode consisting of unheated dye-doped TG and MWCNTs. The photocurrent was generated by excitation of the dye and was enhanced by the CNTs.

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