Preparation and Photocurrent Generation of Nanostructured SnO_2 Films Chemically Modified with Mono-substituted C_{60}-Malonic Acid

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Mono-substituted C_{60}-malonic acid ($C_{60}C(COOH)_2$) was chemically adsorbed on nanostructured SnO_2 electrodes prepared by spincoating ITO substrates with a SnO_2 colloidal suspension followed by thermal annealing at 673 K for 1 h. The photocurrent of the film in a redox electrolyte (I_3^-/I^-) was observed under visible light irradiation or simulated AM1.5G solar irradiation.

Photoelectrochemical and photovoltaic properties of thin films containing fullerene derivatives have attracted much attention because of their interesting photophysical and electrochemical properties. Chemical modification of conductive substrates with photoelectrochemically active materials is a useful method for developing photovoltaic cells where efficient charge injection is expected owing to the chemical connection. In dye-sensitized solar cells, carboxyl groups of a ruthenium dye are directly anchored to the TiO_2 porous electrode.[1] Consequently, an electron from the dye in the excited state is efficiently injected into the conduction band of the electrode. This is one of the reasons why dye-sensitized solar cells have higher conversion efficiency than any other organic solar cell. On the other hand, Kamat et al. reported photoelectrochemical activities of C_{60} clusters electrodeposited on nanostructured SnO_2 films where $(C_{60})_n^-$ is formed by the photoinduced electron transfer between C_{60} clusters and I^- and subsequently an electron of $(C_{60})_n^-$ is transferred to the conduction band of SnO_2.[2,3] However, the electrodeposited C_{60} clusters easily slough off from the substrate because of physisorption. Here we fabricated nanostructured SnO_2 films chemically modified with mono-substituted C_{60}-malonic acid ($C_{60}C(COOH)_2$) activated by dicyclohexylcarbodiimide (DCC) condensing agent and 1*H*-benzotriazol-1-ol (BtOH) additive, and observed the photocurrent generation in the films.

Nanostructured SnO_2 films were prepared as follows. Quartz substrates and ITO-coated substrates (10 Ω per square) were ultrasonicated in toluene, acetone, and ethanol for 10 min and then dried with N_2. The substrates were subsequently cleaned with a UV–O_3 cleaner for 1 h. The cleaned substrates were spincoated with a colloidal SnO_2 suspension. The SnO_2-coated substrates were annealed at 673 K for 1 h. Figure 1 shows the absorption spectra of the SnO_2-coated quartz substrates, obtained by spincoating with SnO_2 colloidal suspensions at various weight concentrations. Absorption at wavelengths shorter than 300 nm ascribable to SnO_2 increased with the SnO_2 concentration, indicating that the thickness of SnO_2-coated films can be controlled by the SnO_2 concentration. The thickness of the SnO_2-coated films was quantitatively evaluated by AFM measurement: 180 nm for the film prepared with a 10 wt % colloidal suspension.

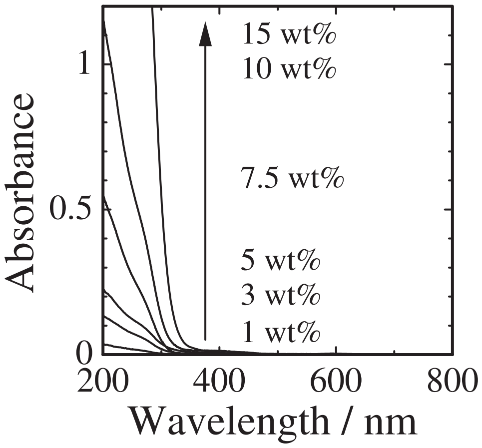

Figure 1. Absorption spectra of SnO_2-coated quartz substrates obtained by spincoating with SnO_2 colloidal suspensions at various concentrations.

By the DCC–BtOH reaction the nanostructured SnO_2 films were chemically modified with $C_{60}C(COOH)_2$,[4,5] which was synthesized as reported previously.[6–8] Before the chemical modification, the SnO_2-coated substrates were cleaned again as mentioned above. The cleaned substrates were immersed in a 50 mL bromobenzene solution with 2.5 μmol $C_{60}C(COOH)_2$ and 2.5 μmol BtOH at 0 °C. Immediately, 2.5 μmol DCC was added to the solution, which was left with slight stirring at room temperature. The substrates were ultrasonicated in bromobenzene for 3 min to remove unreacted species. Figure 2 shows absorption spectra of the SnO_2-coated quartz substrates after chemical

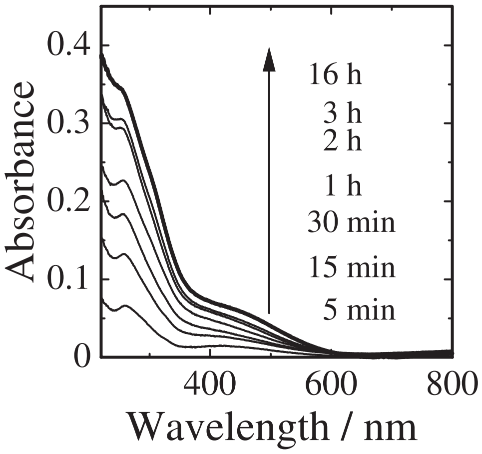

Figure 2. Absorption spectra of SnO_2-coated quartz substrates chemically modified with $C_{60}C(COOH)_2$ for periods indicated.

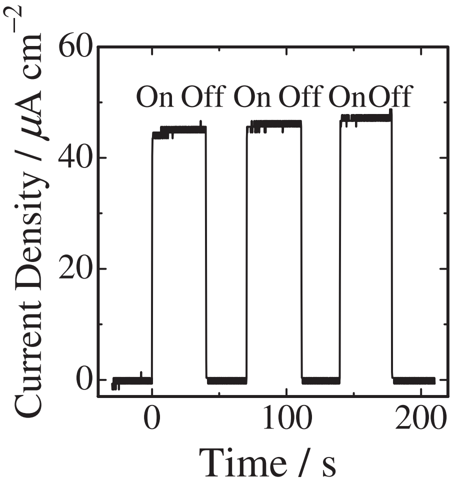

Figure 3. Photocurrent generation in nanostructured SnO_2 film chemically modified with $C_{60}C(COOH)_2$ under visible light irradiation at an intensity of 55 mW cm^{-2}.

modification with $C_{60}C(COOH)_2$ for 5 min to 16 h. Absorption bands observed at wavelengths shorter than 600 nm were ascribed to $C_{60}C(COOH)_2$ from the comparison with those in methanol. As shown in the figure, the modification was almost completed by 3 h, but a slight increase was still observed at 16 h. This probably reflects the time for $C_{60}C(COOH)_2$ molecules to penetrate deeply into the SnO_2-coated film owing to the porous structure. The amount of $C_{60}C(COOH)_2$ chemically adsorbed on the film was estimated to be 3×10^{-9} mol cm^{-2} by the absorption spectrum, which was about 20-fold that on a flat quartz substrate.

Photocurrent generation in the nanostructured SnO_2 film chemically modified with $C_{60}C(COOH)_2$ was measured with a potentiostat (Perkin Elmer, 273A), a three-electrode electrochemical cell with a 0.95-cm^2 window for mounting the substrates as a working electrode, and a 500-W Xe lamp (Oriel) with optical cut filters (L-38 and IRQ-80) and a monochrometor (Oriel, Cornerstone 130). The reference and counter electrodes were an Ag/AgCl electrode with a saturated KCl aqueous solution and a Pt net, respectively. Electrolyte solution was an acetonitrile solution with 0.5 M LiI and 1 mM I_2. The nanostructured SnO_2 films used for the photocurrent measurement were prepared by double coating with a 15 wt % SnO_2 colloidal suspension, which gave a SnO_2-coated film 600 nm in thickness. Figure 3 shows the photocurrent responses of the nanostructured SnO_2 film chemically modified with $C_{60}C(COOH)_2$ under visible light irradiation ranging from 400 to 800 nm with a light intensity of 55 mW cm^{-2}. The film potential was fixed at 0 V vs Ag/AgCl. Prompt and steady photocurrent responses were repetitively observed during several on/off cycles of visible light irradiation while only a slight response was observed for the SnO_2 substrate without $C_{60}C(COOH)_2$. The action spectrum of the photocurrent generation was in agreement with the absorption spectrum of the film, indicating that the photocurrent originates from photoexcitation of $C_{60}C(COOH)_2$ deposited on the SnO_2 porous substrate.

Figure 4 shows *I–V* characteristics of the SnO_2-coated ITO substrate chemically modified with $C_{60}C(COOH)_2$ measured with a two-electrode electrochemical cell under simulated AM1.5G solar irradiation at 100 mW cm^{-2}. The broken curve shows *I–V* characteristics of the chemically modified substrate under a dark condition. The increase in current density seen above 0.2 V is ascribed to the oxidation of I_2. Under irradiation of AM1.5G solar-simulated light, a short-circuit photocurrent of 0.15 mA cm^{-2}, an open-circuit voltage of 0.25 V, and fill factor of 0.4 were obtained. Thus, the solar energy conversion efficiency was calculated to be about 0.015%. Although the amount of adsorbed $C_{60}C(COOH)_2$ was less than that of electrodeposited films, a large short-circuit photocurrent was observed, indicating that electron injection from $C_{60}C(COOH)_2$ to SnO_2 is efficient owing to the chemical connection. It will be further improved by a combination of the chemically modified SnO_2 films with an appropriate light-harvesting molecule.

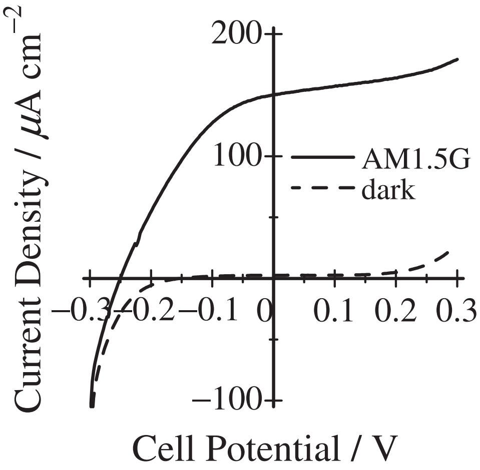

Figure 4. *I–V* characteristics of nanostructured SnO_2 film chemically modified with $C_{60}C(COOH)_2$ under simulated AM1.5G solar irradiation at 100 mW cm^{-2}.

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