Photoconductive properties of TiO_2 films prepared by the sol–gel method and its application

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The Photoconductive characteristics of TiO_2 films prepared by the sol-gel method, and the photovoltaic characteristics fabricated with the resulting TiO_2 film and phthalocyanine nickel (NiPc) are investigated. For a TiO_2 film with hydroxypropyl cellulose (Hpc) heat treated at 500 °C for 10 min, the relative sensitivity is about ten times higher than that without Hpc. A space-charge-limited current is observed in the dark current–voltage characteristic of the TiO_2 film with Hpc. It is found that the TiO_2 film with Hpc has a photosensitizing effect. The photovoltaic characteristics of TiO_2(Hpc)/NiPc are as follows: the short-circuit current density, J_{sc} is 5.6×10^{-7} A cm^{-2}, the open-circuit voltage, V_{oc} is 0.24 V, the fill factor (F.F) is 0.64 and the power conversion efficiency, η is 0.73. Furthermore, the carrier transport mechanisms of the TiO_2(Hpc)/NiPc photovoltaic cell are discussed.

1. Introduction

The remarkable progress of scientific technologies in recent years has made extremely high demands on material. The active development of new materials having a high functionality is being studied. The sol–gel method has attracted special interest recently in the preparation technology of new materials which are prepared by combining inorganic and organic materials [1, 2].

Among such materials, titanium oxide (TiO_2) has been considered to be a photoconductive material [3], and is one of the *n*-type semiconductors most applicable to photochemical electrodes for solar energy conversion into other forms of energy such as H_2 gas and electricity [4, 5]. Further, a phthalocyanine which is a weather-proof organic semiconductor is attracting attention, and its photovoltaic properties [6–8], the effects of dopant materials [9], the effects of metal electrodes [10], etc., have been examined in detail.

In this paper, the effects of the addition of hydroxypropyl cellulose (Hpc) on the photoconductive characteristics of the TiO_2 film prepared by the sol-gel method, and on the photovoltaic characteristics of the resulting TiO_2 film and phthalocyanine nickel (NiPc) were investigated.

2. Experimental procedure

2.1. Preparation of samples

Tetraisopropyl orthotitanate ($[(CH_3)_2CHO]_4Ti$) from Tokyo Kasei Organic Chemicals was used as the metal alkoxide. First, tetraisopropyl orthotitanate (14.7 ml) was added to anhydrous ethyl alcohol (11.7 ml) and was mixed with it by stirring at room temperature. Secondly, anhydrous ethyl alcohol (11.7 ml) was added to H_2O (0.9 ml) and HCl (0.12 ml) at 0 °C, and an alcoholic solution was prepared. The TiO_2 sol solution was prepared by gradual addition of the alcoholic solution using a burette into the mixed titanium alkoxide solution at room temperature. The TiO_2 gel film was obtained by dipping a glass substrate in the TiO_2 sol solution and subsequently pulling it upwards at a constant speed of 1.5 mm sec^{-1}. Finally, the resulting TiO_2 gel film was subjected to heat treatment at 500 °C for 10–30 min. By repeating the above operation three times, a TiO_2 film of 1–3 μm thickness was prepared. In addition, to ensure that TiO_2 film obtained was uniform and adhesive, and to facilitate preparation of TiO_2 composite materials, 1 wt% of hydroxypropyl cellulose (Hpc) was added to the titanium alkoxide solution. Then, a pair of comb-shaped Ag–In electrodes (electrode distance, about 0.37 mm; effective length, 10.8 mm) was vacuum deposited for measurements of the photoconductive properties of the TiO_2 film. Photovoltaic cells of the TiO_2 film were prepared using the sol–gel method; the TiO_2 film was prepared by dipping according to the above operation, and Ag–In electrodes were vacuum deposited on the glass substrate. Phthalocyanine nickel (NiPc) (Tokyo Kasei Organic Chemicals) was vacuum deposited on the glass substrate with the TiO_2 film at 10^{-6} Torr. The thickness of the NiPc film was 100 nm. Moreover, an upper Au electrode was vacuum deposited in the same apparatus. Fig. 1 shows a schematic diagram of the TiO_2/NiPc photovoltaic cell. A photovoltaic cell of Schottky barrier type (Al/NiPc) was formed between NiPc and aluminium on an indium tin oxide (ITO) substrate for comparison with the TiO_2/NiPc photovoltaic cell.

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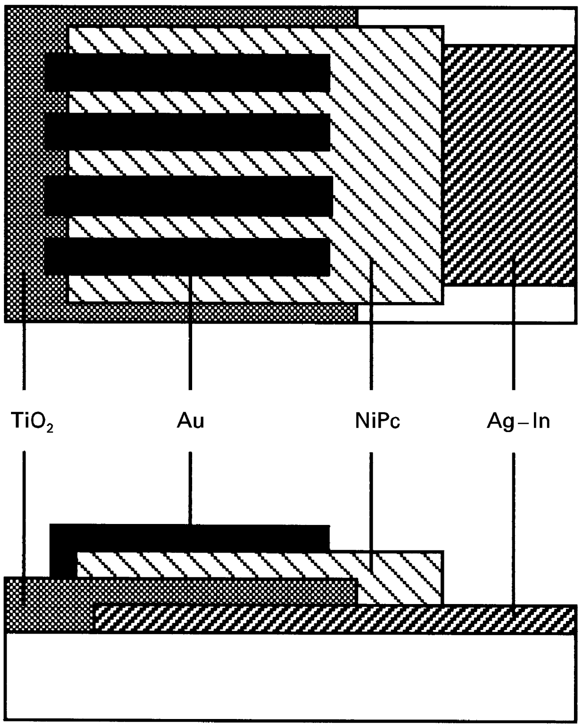

Figure 1 A schematic diagram of the preparation of a TiO_2 film on a glass substrate.

2.2. Electrical measurements

The sample for measurement was placed in a black box which was electrically shielded. The sample was satisfactorily kept in a dry air flow in the dark and thereafter was measured. The photoconductive properties, the dark current–voltage properties and the photovoltaic properties were measured by the use of an electrometer (TR-8652, Advantest Co. Ltd). The values of the dark current and the photocurrent were measured at a constant applied voltage of 10 V DC, and the dark current–voltage characteristics were measured at the applied voltage in the range 1–150 V. The sample was irradiated with monochromatic light through a monochromator (G-250, Nikon) with a xenon lamp (UXL-500D, Ushio Denki) as the light source, and with the light in the basic absorption region (425 nm) of TiO_2 for measurements of the photoconductive properties. The values of the photocurrent in the action spectrum were normalized by the incident light intensity of various wavelengths. The light intensity was varied using a neutral density filter (ND filter, Vacuum Optics Corporation of Japan). The light intensity was measured by the use of a radio meter (DR-2000, EG&G Gamma Scientific). A power conversion coefficient was calculated by consideration of the light transmission factor on the electrode.

3. Results and discussion

3.1. Photoconductivities of the TiO_2 films

The photoconductivities of the TiO_2 films prepared by the sol–gel method are shown in Table I. Here, the relative sensitivity is represented by dividing the photocurrent, I_p, by the dark current, I_d. We found that the TiO_2 films had no defects (i.e., no pinholes, no cracks nor exfoliation) and were not transparent [11]. The relative sensitivity of the TiO_2 film is similar to that of polycrystalline TiO_2. [3, 12]. On the other hand, it is recognized that the TiO_2 film with Hpc tends to increase the dark current, the photocurrent and the relative sensitivity. The relative sensitivity of the TiO_2 film with Hpc heat treated at 500 °C for 10 min increases about ten times in comparison with that of the TiO_2 film without Hpc. Therefore, it is found that the TiO_2 film with Hpc has a light-sensitive effect, and that the increase in the photoconductivity is due to the addition of Hpc as a viscous agent. Further, Hpc molecules with TiO_2 particles at their centres is expected to be oriented by heat treatment for a relatively short time. Consequently, it seemed that the photoconductivity of the TiO_2 film with Hpc increases owing to enhancement of the interfacial interaction between TiO_2 and Hpc, and that a special molecular aggregation of Hpc on the TiO_2 occurs [13]. However, it is considered that Hpc is gradually oxidized and decomposed on increasing the heat treatment time, and the light-sensitive effect decreases. The experimental results also suggest this tendency.

3.2. Dark current–voltage characteristics of the TiO_2 films

Dark current–voltage characteristics of the TiO_2 films are shown in Fig. 2. The TiO_2 film is characterized by the fact that it obeys Ohm's law ($J \propto V^n$, where $n \approx 1$, J is the current density and V is the applied voltage) in the voltage range 2–150 V. Meanwhile, the TiO_2 film with Hpc also obeys Ohm's law in the voltage range 2–30 V and shows an exponential dependence on the voltage in the voltage range above 30 V. The dark current–voltage characteristics are similar to those obtained by Cardon. [14]. The exponential dependence of the dark current suggests a space-charge-

TABLE I Photoconductivities of the TiO_2 films prepared by the sol–gel method

Film	Heat treatment		Dark current I_d (A)	Photocurrent I_p (A)	Relative sensitivity I_p/I_d
	Temperature (°C)	Time (min)			
TiO_2	500	10	4.2×10^{-12}	9.1×10^{-10}	2.2×10^2
TiO_2 + 1 wt % Hpc	500	10	2.8×10^{-11}	6.2×10^{-8}	2.3×10^3
TiO_2 + 1 wt % Hpc	500	30	3.3×10^{-11}	2.4×10^{-8}	7.3×10^2

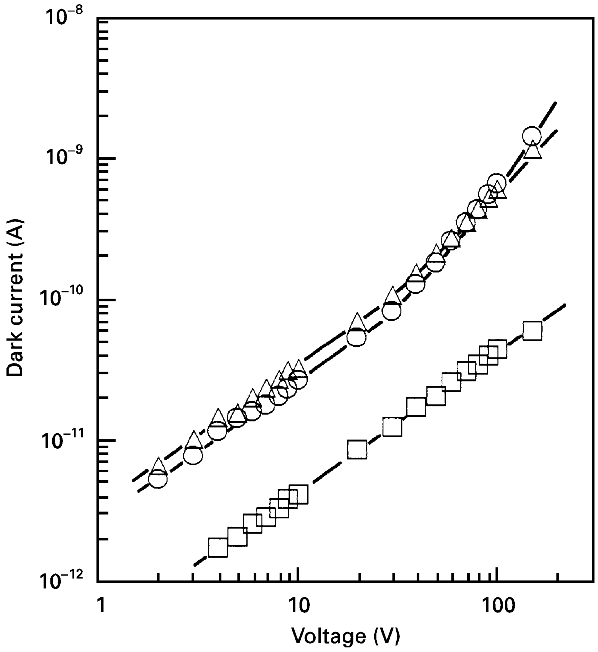

Figure 2 Dark current–voltage characteristics of the TiO_2 films for various heat treatments. (□) 500 °C, 10 min; (○) 1 wt % Hpc, 500 °C, 10 min; (△) 1 wt % Hpc, 500 °C, 30 min.

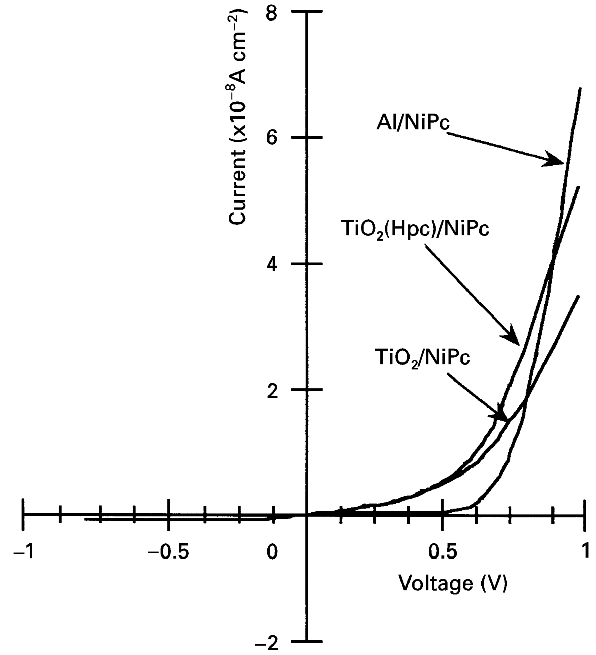

Figure 3 Dark current–voltage characteristics of the TiO_2/NiPc, TiO_2(Hpc)/NiPc and the Al/NiPc photovoltaic cells.

limited current. This seem to depend largely on the total trapped electron density in the sample. It is well known that the phenomena include field emission from electrodes, traps or the valence band, collision ionization of trapped or valence electrons, poor contact, barriers, and heating effects. Although the effects in the TiO_2 film with Hpc are not completely understood, it is reasonable to assume that they are due to the migration of O vacancies under the influence of the applied voltage to the negative electrode and heating effects. Therefore, it is considered that the photosensitizing effect is due to increasing the trapped density.

3.3. Dark current–voltage properties of the photovoltaic cells

Fig. 3 shows the dark current–voltage characteristics of the TiO_2/NiPc, TiO_2(Hpc)/NiPc and Al/NiPc photovoltaic cells. When a positive bias was applied, to the Ag–In and ITO electrodes, a forward voltage occurred. As shown in Fig. 3, the dark current–voltage characteristics indicated good rectification for all cells. The rectification ratios were about 12, 28 and 130 at 0.7 V for TiO_2/NiPc, TiO_2(Hpc)/NiPc and Al/NiPc, respectively. As a result, the rectification rate for Al/NiPc is similar to that obtained by Misoh *et al.* [15], and those of TiO_2/NiPc and TiO_2(Hpc)/NiPc were low. This may be due to the imperfect formation of the heterojunction at the interface between the TiO_2 and NiPc. However, the TiO_2(Hpc)/NiPc photovoltaic characteristics were higher than those of Al/NiPc. As mentioned above, this seems to indicate that the TiO_2 film with Hpc has a light-sensitive effect.

The forward dark current–voltage characteristics for the TiO_2(Hpc)/NiPc photovoltaic cell at various temperatures from 253 to 313 K are shown on

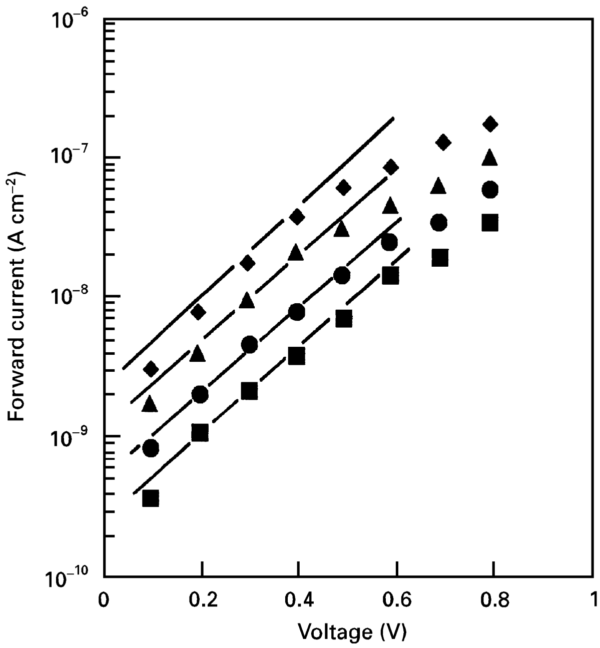

Figure 4 The forward dark current–voltage characteristics for the TiO_2(Hpc)/NiPc photovoltaic cell at various temperatures from 253 to 313 K. (■) 253 K; (●) 273 K; (▲) 293 K; (◆) 313 K.

a semilogarithmic plot in Fig. 4. The TiO_2(Hpc)/NiPc photovoltaic cell shows that the dark current has an exponential behaviour in the range of 0.1–0.4 V and deviates from this behaviour for voltages above 0.4 V. This seems to be due to the series resistance.

A diode characteristic is generally described by the standard diode equation as follows:

$$J = J_0 \exp\left(\frac{qV}{nkT}\right) \quad (1)$$

where J is the current density, J_0 is the saturation current density at the reverse bias voltage, q is

TABLE II Diode factor, n, and tunneling constant, A, at various temperatures for the TiO_2(Hpc)/NiPc photovoltaic cell

Temperature (°C)	J_0 ($A\,cm^{-2}$)	n	A
253	2.75×10^{-10}	6.54	7.0
273	5.00×10^{-10}	6.45	7.0
293	1.25×10^{-9}	5.00	7.2
313	2.30×10^{-9}	5.00	7.4

a charge of an electron, V is the forward bias voltage, n is the diode factor, k is Boltzmann's constant and T is the absolute temperature. The diode factor n was estimated from the forward dark current–voltage (J–V) characteristics for the TiO_2(Hpc)/NiPc photovoltaic cell at various temperatures using equation (1); these results are shown in Table II. As shown in Table II, n varies from 5.00 to 6.54 within the experimental temperature range. However, the gradients of the semilogarithmic plots of the J–V characteristics are approximately parallel. Therefore, it is suggested that the J–V characteristics for the TiO_2(Hpc)/NiPc photovoltaic cell are dominated by the current transport mechanisms consisting of a tunnelling process [12, 16, 17]. The forward current in the tunnelling process is related to the voltage by the following equation [12, 17]:

$$J = J_t \exp[A(V - V_d)] = J_0(T)\exp(AV) \qquad (2)$$

where J_t depends on the density of traps, $J_0(T)$ is the extrapolated intercept which has an exponential dependence on the built-in potential, V_d, of the junction, and A is the tunnelling constant. The values of the tunnelling constant, A, at various temperatures together with the corresponding values of the diode factor, n, are obtained by fitting the J–V data to the standard diode equation. However, A remains almost unchanged over the temperature range considered, with average values of 7.2 V^{-1}. Consequently, it seems that the temperature dependence of A is very small. We are to led to the conclusion that the J–V characteristics for the TiO_2(Hpc)/NiPc photovoltaic cell are not consistent with Equation 1 but are consistent with Equation 2. In addition, as shown in Fig. 5 the temperature dependence of the reverse saturation current density shows that ln J_0 changes linearly with increasing temperature. These results obtained also support the above-mentioned current transport mechanism which consists of a tunnelling process through the junction.

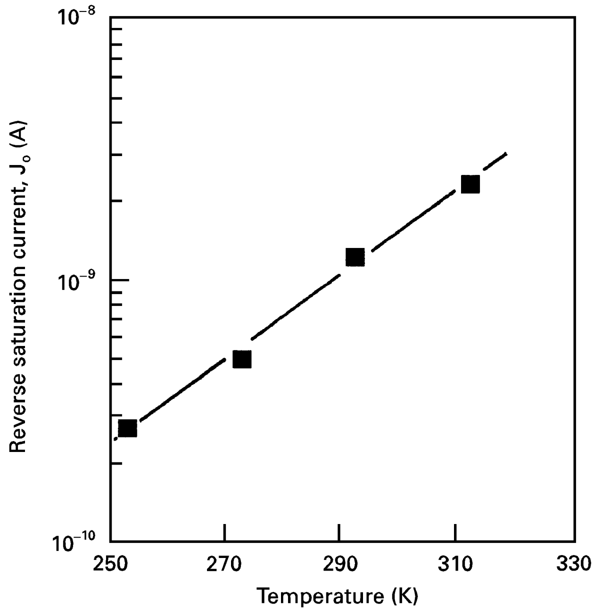

Figure 5 Temperature dependence of the reverse saturation current density.

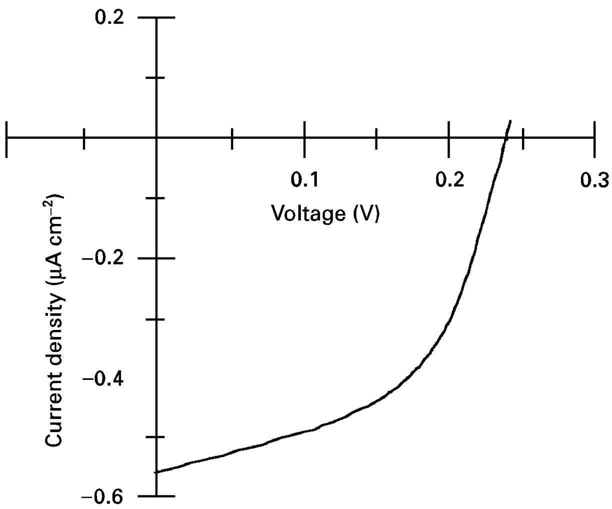

Figure 6 J–V characteristic of TiO_2(Hpc)/NiPc irradiated with light of 550 nm wavelength through an Ag–In electrode on the glass substrate side.

TABLE III Photovoltaic parameters of J_{sc}, V_{oc}, FF and η for Al/NiPc and TiO_2(Hpc)/NiPc photovoltaic cells

	J_{sc} ($A\,cm^{-2}$)	V_{oc} (V)	FF	η (%)
Al/NiPc	4.7×10^{-8}	0.48	0.37	0.083
TiO_2(Hpc)/NiPc	5.6×10^{-7}	0.24	0.54	0.73

3.4. Photovoltaic characteristics

Fig. 6 shows J–V characteristic of TiO_2(Hpc)/NiPc irradiated with light of 550 nm wavelength through the Ag–In electrode on the glass substrate side. As shown in Table III the photovoltaic characteristics of TiO_2(Hpc)/NiPc were as follows: the short-circuit current density, J_{sc} is 5.6×10^{-7} $A\,cm^{-2}$, the open-circuit voltage, V_{oc} is 0.24 V, the fill factor (FF) is 0.54 and the power conversion efficiency, η, is 0.73. The power conversion efficiency, η, was calculated from the following equation:

$$\eta = \frac{J_{sc}V_{oc}\,\mathrm{FF}}{P_w} \times 100\% \qquad (3)$$

where P_w is the value of the light intensity obtained by considering the transmission factor of the electrode. The transmitted light through the Ag–In electrode was about 10% of the incident light. Although the

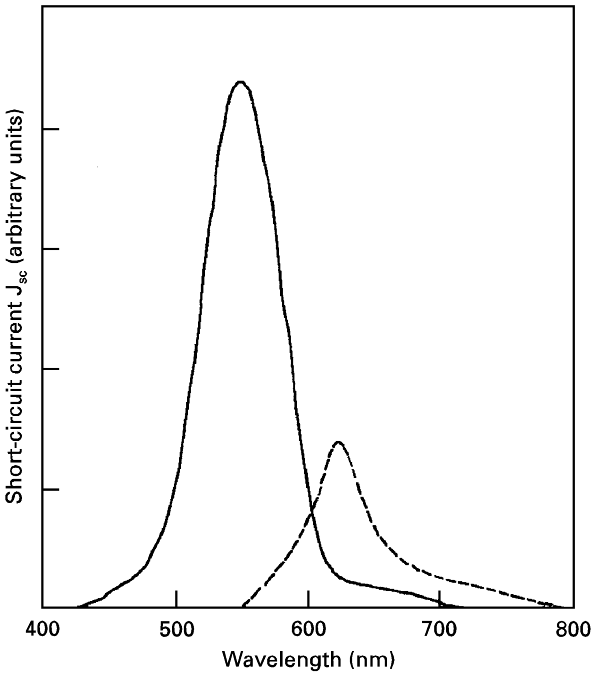

Figure 7 The dependence of the short-circuit current on the wavelength for TiO_2(Hpc)/NiPc (——) and Al/NiPc (– – – –).

rectification ratio of the dark current-voltage characteristics for TiO_2(Hpc)/NiPc is not necessarily a sufficiently high value, it is found that the photovoltaic parameter has been considerably improved. The reason seems to be that the TiO_2 film with Hpc has a light-sensitive effect.

Fig. 7 shows the dependence of the short-circuit current on the wavelength for TiO_2(Hpc)/NiPc and Al/NiPc. As a result, the action spectrum of Al/NiPc was in agreement with the basic absorption spectrum of NiPc, and that of TiO_2(Hpc)/NiPc; however, it was different from the basic absorption spectrum of TiO_2 and NiPc and showed a peak at about 550 nm. TiO_2 and NiPc are photosensitive at about 415 nm (3.0 eV) and 630 nm (1.97 eV), respectively. Therefore, it is considered that the maximum action spectrum of TiO_2(Hpc)/NiPc is due to the effective use of TiO_2 as a window layer in the short-wavelength range.

The dependences of the short-circuit current density, J_{sc}, and open-circuit voltage, V_{oc}, on the light intensity for TiO_2(Hpc)/NiPc are shown in Fig. 8. V_{oc} has a tendency to saturate with increasing light intensity in the experimental light intensity ranges. On the other hand, J_{sc} is characterized by the fact that it obeys $J_{sc} \propto L^m$ (where L is the light intensity and m is a constant). $m \approx 0.72$ is calculated from the characteristics, and J_{sc} has a sublinear behaviour. Therefore, it is considered that carrier traps exist in the TiO_2 film, and that recombination between electrons and holes through the carrier traps increases with increasing light intensity [18].

The dependence of the power conversion efficiency on the light intensity for TiO_2(Hpc)/NiPc is shown in Fig. 9. The power conversion efficiency decreases with increasing light intensity. This seems to be caused by the fact that J_{sc} does not increase with increasing light intensity.

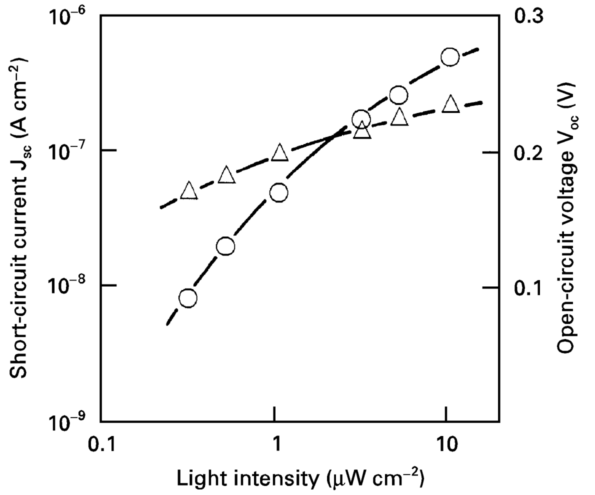

Figure 8 The dependences of the short-circuit current density J_{sc} (○) and open-circuit voltage V_{oc} (△) on the light intensity for TiO_2(Hpc)/NiPc.

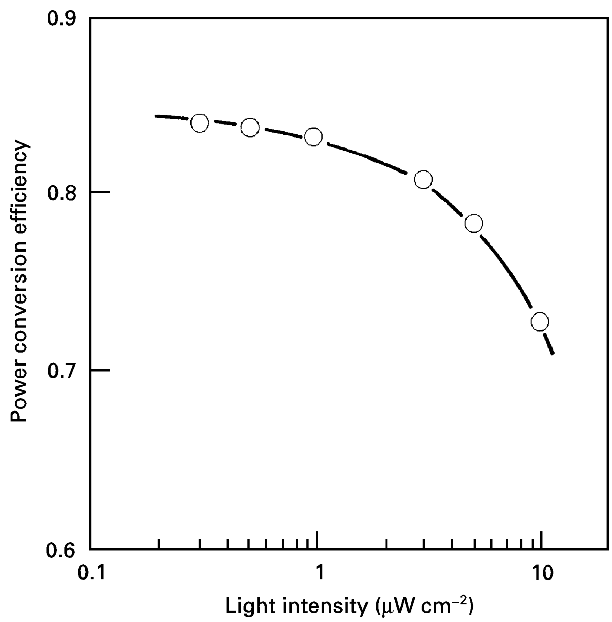

Figure 9 The dependence of the power conversion efficiency on the light intensity for TiO_2(Hpc)/NiPc.

4. Conclusion

The photoconductivities of TiO_2 films prepared by the sol–gel method were investigated. As a result, the dark current, the photocurrent and the relative sensitivity of the TiO_2 film with Hpc are increased. A space-charge-limited current is observed in the dark current–voltage characteristic of the TiO_2 film with Hpc. It is considered that the interfacial interaction between TiO_2 and Hpc is enhanced, a special molecular aggregation of Hpc on the TiO_2 is formed at such interfaces, an electron depletion occurs or an electron-enriched layer is formed. Photovoltaic cells fabricated with the TiO_2 film with Hpc which has a photosensitive effect and NiPc are investigated. The photovoltaic characteristics of TiO_2(Hpc)/NiPc are as follows: the short-current density, J_{sc} is 5.6×10^{-7} A cm^{-2}, the open-circuit voltage, V_{oc}, is 0.24 V, the FF is 0.54 and the power conversion efficiency, η, is

0.73. The action spectrum of TiO_2(Hpc)/NiPc was different from the basic absorption spectrum of TiO_2 and NiPc and showed a peak at about 550 nm. It is considered, therefore, that the maximum action spectrum of TiO_2(Hpc)/NiPc is due to the effective use of TiO_2 as a window layer in the short-wavelength range.

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