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Photoelectrochemical Properties of a Porous Nb_2O_5 Electrode Sensitized by a Ruthenium Dye

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In studying the photoelectrochemical properties of TiO_2, Nb_2O_5, ZnO, SnO_2, In_2O_3, WO_3, Ta_2O_5, and ZrO_2 porous semiconductor films sensitized by the ruthenium(II) *cis*-bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) complex, it was found that the Nb_2O_5 semiconductor cell had the next highest incident of monochromatic photon-to-current efficiency (IPCE = 18%) compared to the TiO_2 cell and showed the highest open-circuit photovoltage (V_{oc}) among them. The V_{oc} of the dye-sensitized cell was proved to be related to the flatband potential of the semiconductor electrode. The Ru dye adhered to the Nb_2O_5 surface mainly through an ester-like linkage. It is speculated that electrons are transferred mainly through the conjugated orbitals of the ester linkage and semiconductor conduction band and that the TiO_2 and Nb_2O_5 conduction bands consisting of d-orbitals are more advantageous than those of s-orbitals in attaining the desired IPCE. The IPCE of the Nb_2O_5 cell was markedly improved by treating the Nb_2O_5 electrode with Nb alkoxide, and the maximum IPCE was 32% at 548 nm. The overall solar-to-electric energy conversion efficiency was about 2% (AM-1.5, 100 mW/cm^2).

Introduction

Dye sensitization of porous wide-band gap semiconductor electrodes has been intensively studied in attempts to make photoelectrochemical solar cells more efficient. The most efficient cell reported thus far was based on a porous TiO_2 semiconductor film sensitized by an adsorbed Ru−complex molecule monolayer.[1,2] This cell had a 10% solar-to-electric energy conversion efficiency and >80% incident monochromatic photon-to-current efficiency (IPCE). The keys to this high efficiency are, first, that a large number of dye molecules directly adhere to the semiconductor surface due to the high surface area of the semiconductor film and, second, that the Ru dye, ruthenium(II) *cis*-bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid), absorbs most photons in the visible light region (∼800 nm) and effectively injects electrons into the semiconductor conduction band. Most research work has focused on investigation of the electron-transfer rate and sensitizer optimization using a porous TiO_2 semiconductor film, but little attention has been focused on other semiconductor films. Some porous semiconductor films such as ZnO,[3,4] $SrTiO_3$,[5] and SnO_2[6] have been reported in photoelectrochemical solar cells using several different Ru dye sensitizers; however, their total light conversion efficiency was low compared to that of the TiO_2 cell. A semiconductor has inherent properties such as band gap, conduction and valence band potentials, and crystal and surface structures. It is worthwhile to investigate different semiconductors for a fundamental understanding of the dye-sensitized solar cell systems.

In this study, we describe the photoelectrochemical characterization of different types of porous semiconductor films with an adsorbed layer of ruthenium(II) *cis*-bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) complex as a sensitizer. We focused on a dye-sensitized Nb_2O_5 semiconductor cell which showed the next highest IPCE to the TiO_2 cell and the highest open-circuit photovoltage (V_{oc}) among all the semiconductor cells we tested.

Experimental Section

1. Preparation of Porous Semiconductor Film. Porous semiconductor films were prepared by coating a conducting glass support (Nihon Sheet Glass Co.; fluorine-doped SnO_2 overlayer; sheet resistance: 10 Ω/sq) with a viscous slurry of semiconductor powder dispersed in an aqueous solution. The types of semiconductor oxide powders used were commercial Nb_2O_5 powder (Wako Chemical, Aldrich, or Kishida Chemical) and in-house Nb_2O_5 powder prepared by calcining niobium hydroxide (Central Glass Co. or Mitsui Kinzoku Co.) in air between 300 and 900 °C. Niobium hydroxide was also produced by hydrolysis of $NbCl_5$ (Wako Chemical) or $Nb(OC_2H_5)_5$ (Cerac Co., 99.999%) using a 1% HNO_3 aqueous solution. Nb_2O_5 powder (2.0 g) was ground in a mortar with distilled water (typically 4 mL), acetylacetone (10 μL), and Triton X-100 (50 μL, Aldrich) to break up the aggregate into

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Table 1. Photoelectrochemical Properties of Several Types of Porous Semiconductor Solar Cells Sensitized by $(NCS)_2RuL_2$ Dye[a]

semiconductor	V_{oc}, V	I_{sc}, mA	fill factor, %	IPCE, %	absorption peak, nm	surface area,[e] m^2/g of semiconductor
TiO_2 (Aerosil)[b]	0.52	0.73	57	45	545	45
Nb_2O_5 (from $Nb(OH)_5$)[c]	0.61	0.29	58	545	100	
ZnO (Wako)[b]	0.49	0.11	28	7	510	30
SnO_2 (Wako)[b]	0.32	0.19	30	12	540	60
WO_3 (from H_2WO_4)[d]	0.31	0.11	26	7	535	20
In_2O_3 (Wako)[b]	0.25	0.10	31	6	545	25
ZrO_2 (Aerosil)[b]		tr		0	535	90
Ta_2O_5 (Kanto)[b]		tr		0		5

[a] All semiconductor powders were precalcined at 500 °C for 1 h in air. Semiconductor film thickness = 6−8 μm. Solar cell efficiency was measured under monochromatic light through a band-pass filter (520 nm, 4 mW/cm^2). Semiconductor film electrode area = 1 × 1 cm. Irradiation area = 1 × 1 cm. [b] Commercialized oxide powder. [c] The $Nb(OH)_5$ precursor (Central Glass Co.) was calcined at 500 °C for 1 h in air. [d] The H_2WO_4 precursor (Kanto Chemical Co.) was calcined at 500 °C for 1 h in air. [e] Powder samples were measured after precalcination at 500 °C for 1 h in air.

a dispersed paste. Adhesive tape (standard thickness: 60 μm) was placed on the edges of the conductive glass to form a guide for spreading the slurry using a glass rod. The film thickness was controlled by the amount of water in the slurry and by the adhesive tape thickness. After being dried in air, the semiconductor film on conducting glass was calcined for 1 h at 500 °C in air. The film thickness was measured after film calcination using a Tencor Instruments Alpha-Step 300 apparatus. Commercial TiO_2 powder (P25, Nihon Aerosil), reported to be highly efficient,[2] was used for the TiO_2 film, which was prepared using the same method as the Nb_2O_5 film. ZnO, SnO_2, ZrO_2, Ta_2O_5, and In_2O_3 semiconductor powders were prepared by hydrolysis of metal chloride or alkoxide precursors and were also obtained commercially. The film preparation of these semiconductors was the same as for the Nb_2O_5 film. In the case of ZnO, Rensmo's method was also referred.[4] The powder surface area and semiconductor film roughness factor were evaluated by the BET method using nitrogen or krypton gas. The film surface morphology was studied using high-resolution scanning electron microscopy (SEM, Hitach S-800) at 10−15 kV.

2. Sensitization of the Semiconductor Film Electrode. The ruthenium(II) *cis*-bis(thiocyanate)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) complex, hereafter abbreviated as $(NCS)_2RuL_2$, was synthesized in accordance with the published procedures.[2] The purity and structure were confirmed by elemental analysis, IR spectra, and NMR analysis. The dye was adsorbed onto the semiconductor surface by soaking the semiconductor film electrode in a 3 × 10^{-4} mol/L Ru complex solution in dry ethanol. After annealing for 0.5 h at 500 °C in a N_2 atmosphere, the film electrode was cooled to 80 °C and immediately soaked in an 80 °C dye solution. The dye solution was refluxed at 80 °C for 1 h. After dye adsorption, the film electrode was removed from the solution and the photoelectrochemical measurement was conducted immediately. The amount of adsorbed dye was determined by spectroscopic measurement of dye desorbed from the semiconductor surface in a NaOH (0.1 mol/L)-containing mixture of water and ethanol (50:50 by volume).

3. Photoelectrochemical Characterization of the Sensitized Film. The dye-sensitized semiconductor electrode was incorporated into a thin-layer, sandwich solar cell. The area of the semiconductor electrodes was 1 × 1 cm. The counter electrode was a thin platinum layer sputtered on conducting glass. A polyethylene spacer (0.12 mm thickness) was used to prevent the cell from shorting when the counter and working electrodes were clamped together. The electrolyte solution was composed of 0.5 mol/L of tetra-*n*-propylammonium iodide and 0.05 mol/L of iodine in ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume). The dye-coated semiconductor film was illuminated through the conductive glass support using a Xe lamp (500 W, Ushio Denki Co.) as the light source and band-pass filters, e.g., 4 mW/cm^2 for a 520 nm band-pass filter. The overall solar-to-electric energy conversion efficiency was measured under simulated solar light (Wacom Co., WXS-80C-3, AM-1.5, 100 mW/cm^2). The intensity of the illumination source was measured using a power meter with a Si PIN photodiode sensor (Advantest, TQ8210) and a thermopile power meter (Eppley, J3). The photocurrent, photovoltage, and potential−current curve were measured using a potentiostat with a nonresistance ammeter (Nikko Keisoku Co., NPGS-2501) and an XY recorder. Cell characterization data was not corrected for intensity loss due to light passing through the electrode or to glass support reflection.

FTIR spectra were recorded in diffuse-reflectance mode using a Bio-Rad FTS-60 spectrometer with a 2 cm^{-1} resolution.

Results and Discussion

1. Photoelectrochemical Efficiency of $(NCS)_2RuL_2$ Dye-Sensitized Semiconductor Cells. Table 1 shows the light conversion efficiencies of dye-sensitized solar cells composed of several types of porous semiconductor electrodes at 520 nm irradiation. We examined three to five types of oxide powders prepared from several precursors and commercial oxide powders for each semiconductor and determined the best result for each cell. Film thickness was controlled at 6−8 μm. The TiO_2 semiconductor cell showed the highest short-circuit photocurrent (I_{sc}), and the Nb_2O_5 cell prepared from $Nb(OH)_5$ (Central Glass) showed the next highest I_{sc} to the TiO_2 cell. Incident monochromatic photon-to-current efficiency (IPCE) was calculated as follows:

$$\text{IPCE} = \frac{1250 \times \text{photocurrent density } [\mu\text{A/cm}^2]}{\text{wavelength [nm]} \times \text{total incident photon flux } [\text{W/m}^2]} \quad (1)$$

IPCE was 45% for TiO_2 and 18% for Nb_2O_5 cells. Moreover, the fill factor of the Nb_2O_5 cell was as good as that of the TiO_2 cell and much higher than that of other cells.

The open-circuit photovoltage (V_{oc}) of the Nb_2O_5 cell was the highest of all semiconductor cells, including the TiO_2 cell. Figure 1 shows the relationship between the flat-band potential of the oxide semiconductors[7,8] and open-circuit photovoltage of dye-sensitized cells using semiconductor electrodes. The measured V_{oc} values of each semiconductor electrode were within the error bar in Figure 1, and V_{oc} tended to decrease with increasing flatband potential. Figure 2 illustrates the currently accepted mechanism of photosensitization of a wide-

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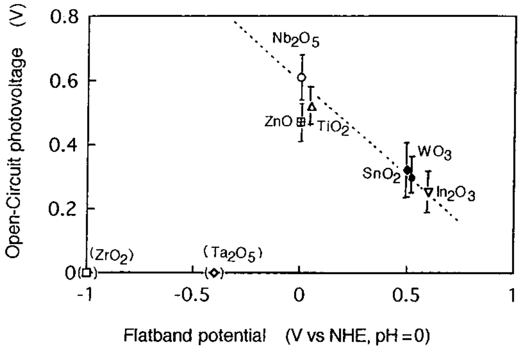

Figure 1. Semiconductor flat-band potentials and the open-circuit photovoltage (V_{oc}) of dye-sensitized semiconductor cells measured under 520 nm monochromatic light. Flatband potentials are from refs 7 and 8.

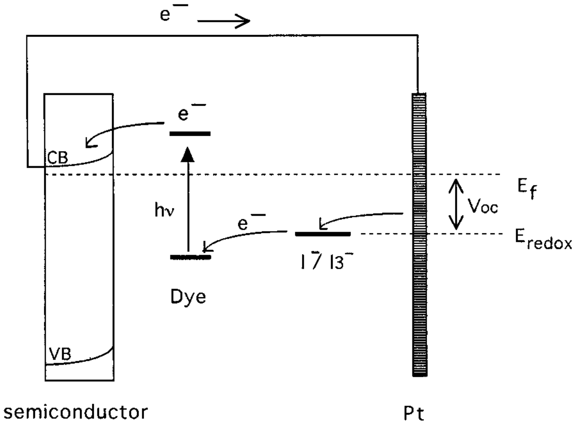

Figure 2. Mechanism of wide-band gap semiconductor photosensitization using adsorbed dye.

band gap semiconductor by an adsorbed dye.[5] Irradiation to the dye promotes the ground state to an excited state. If the oxidation potential of the excited state is located at a more negative potential than the semiconductor conduction band edge, the excited dye transfers an electron to the conduction band of the semiconductor, producing the oxidized dye. The oxidized dye is reduced to the ground state by electron donor I^-. V_{oc} is thus expressed as the difference between the I^-/I_3^- redox potential and the flat band potential close to the n-type semiconductor conduction band. The tendency in Figure 1 agrees with this mechanism except for ZrO_2 and Ta_2O_5. The oxidation potential of the $(NCS)_2RuL_2$ dye was ca. 1.09 V (vs NHE, in acetonitrile) and the threshold of excitation energy was ca. 1.75 eV.[2] Therefore, the oxidation potential of the excited dye is simply estimated to be −0.66 V (vs NHE, in acetonitrile). Even though it is very difficult to predict whether the dye in an excited-state injects electrons into a semiconductor, we speculate that, for ZrO_2 ($E_{fb} = -1.0$ V vs NHE in water pH = 0),[7] the highly negative conduction band potential may be attributable to negligible efficiency. In the case of Ta_2O_5 semiconductor, a good Ta_2O_5 electrode with a high roughness factor could not be prepared in this study, and a very small amount of dye adsorbed on the Ta_2O_5 surface is supposed to be the main reason for its poor efficiency.

Table 2 shows the dependence of photoelectrochemical properties of various Nb_2O_5 cells on the preparation conditions of the Nb_2O_5 electrode. Nb_2O_5 powder prepared by precalcining $Nb(OH)_5$ at 500, 700, and 800 °C in air was coated onto conducting glass at different thicknesses and then calcined again at 500 °C in air. It was found that both the higher the precalcination temperature was and the thinner the Nb_2O_5 film thickness was, the higher the open-circuit photovoltage was; moreover, the maximum V_{oc} was 0.71 V. The photocurrent increased with increasing film thickness up to about 8 μm, then it decreased because thicker films cracked and peeled off easily. Both the Nb_2O_5 powder surface area and the film roughness factor decreased with increasing precalcination temperature; therefore, the amount of adsorbed dye decreased with precalcination temperature. On the other hand, both the Nb_2O_5 film photocurrent and photovoltage increased with precalcination temperature under UV light irradiation in the absence of dye adsorption. It is speculated that the photoconductivity of the Nb_2O_5 particles may thus be improved and physical defects in the semiconductor film may decrease with increasing precalcination temperature. The 8-μm-thick cell precalcined at 700 °C showed the highest photocurrent.

The dependence of short-circuit photocurrent upon light intensity is shown in Figure 3. The photocurrent was proportional to light intensity up to 50 mW/cm^2 and gradually deviated downward from the proportional line (dashed line) at >50 mW/cm^2. It is considered that the diffusion limitation of the electrolyte might be one of the reasons for the decline at high light intensity; however, the actual explanation is uncertain at present.

About 2.8×10^{-8} mol/cm^2 of dye was adsorbed on Nb_2O_5 calcined at 700 °C, one-third of that on TiO_2 (8.1×10^{-8} mol/cm^2). The light-harvesting efficiency (LHE) is calculated as follows:[2]

$$\mathrm{LHE}(\lambda) = 1 - 10^{-\Gamma\sigma(\lambda)} \qquad (2)$$

where Γ is the number of moles of sensitizer per square centimeter (2.8×10^{-8} mol/cm^2 for Nb_2O_5) and σ is the absorption cross section of the dye (1.42×10^7 cm^2/mol). Neglecting reflection and the scattering effect, the LHE of the Nb_2O_5 cell was calculated as 0.60 and that of the TiO_2 cell as 0.93. The low LHE contributed to the low photocurrent efficiency. Moreover, the Nb_2O_5 electrode showed a higher light scattering than the TiO_2 electrode. The scattering efficiency was highest when particle size was half of the incident light wavelength.[9] Most particles of Nb_2O_5 calcined at 700 °C were 100−200 nm (see Figure 8), but some larger particles more than 200 nm were observed by SEM measurement, and these large particles caused high scattering efficiency in the visible light region. The reflected photons scattered outward by semiconductor particles also resulted in the loss of IPCE.

2. Characterization of Dye-Sensitized Semiconductor Cell. Figure 4 shows the absorption spectrum of the $(NCS)_2RuL_2$ dye in an ethanol solution and the diffuse reflectance UV−vis spectra of semiconductor films with and without the Ru dye. The film transmittance could not, however, be measured due to the high light scattering property mentioned above. The UV absorption threshold wavelength of Nb_2O_5 without dye (b) was shorter than that of TiO_2 (a), that is, the Nb_2O_5

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Table 2. Photoelectrochemical Properties of Several Types of Porous Nb_2O_5 Solar Cells Sensitized by $(NCS)_2RuL_2$ Dye and Nonsensitized Cells[a]

precalcination temp, °C	film thickness, μm	V_{oc}, V	I_{sc}, mA	fill factor, %	roughness factor[b]	amount of dye $\times 10^{-8}$ mol/cm^2
			Nb_2O_5 with dye			
500	6	0.61	0.29	58	800	4.7
500	9	0.60	0.29	56		
500	12	0.56	0.27	55		
700	3	0.60	0.10	61		
700	8	0.59	0.32	63	200	2.8
700	10	0.57	0.22	59		
800	4	0.71	0.11	59		
800	8	0.63	0.21	62	120	tr
			Nb_2O_5 (no dye)[c]			
500	7	0.10	0.008	30		−
700	6	0.34	0.025	37		−
800	7	0.30	0.025	35		−

[a] Solar cell efficiency was measured under monochromatic light through a bandpass filter (520 nm, 4 mW/cm^2). Semiconductor film electrode area: 1 × 1 cm. Irradiation area: 1 × 1 cm. Nb_2O_5 powder was prepared from the $Nb(OH)_5$ precursor (Central Glass Co.) by precalcination for 1 h in air. [b] The roughness factor was measured after film preparation. [c] The Nb_2O_5 cell without dye was preformed under whole light from a nonfiltered Xe lamp (NaI/I_2 in H_2O).

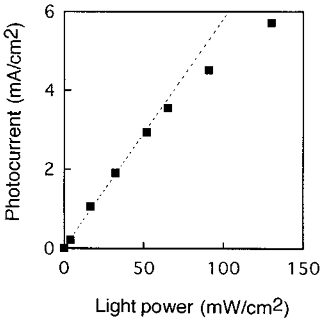

Figure 3. Dependence of short-circuit photocurrent upon the light intensity of $(NCS)_2RuL_2$-sensitized Nb_2O_5 cell (1 × 1 cm). Light source: 500 W Xe lamp with <420 nm cutoff filter. Electrolyte solution: 0.5 mol/L tetra-*n*-propylammonium iodide and 0.05 mol/L iodine in ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume).

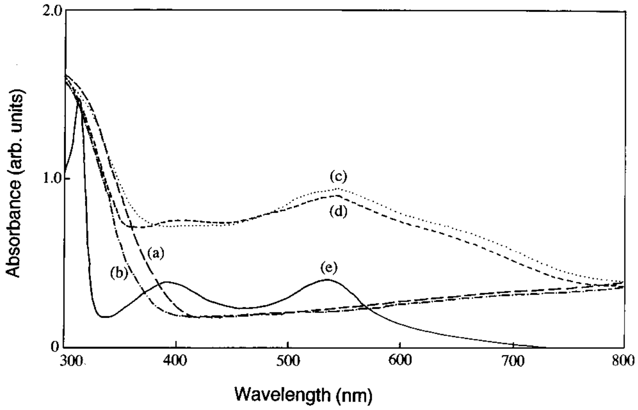

Figure 4. Absorption spectrum of $(NCS)_2RuL_2$ dye in ethanol solution and diffuse reflectance UV−vis spectra of semiconductor films adsorbed with or without Ru dye: (a) TiO_2, (b) Nb_2O_5, (c) $(NCS)_2RuL_2$ on TiO_2, (d) $(NCS)_2RuL_2$ on Nb_2O_5, and (e) $(NCS)_2RuL_2$ in ethanol. Nb_2O_5 powder was precalcined at 500 °C for 1 h.

film electrode had a larger band gap than the TiO_2 electrode. The larger band gap of Nb_2O_5 semiconductor was related to the more negative conduction band potential and the larger open-circuit photovoltage of the Nb_2O_5 cell.

The absorption peaks of the $(NCS)_2RuL_2$ dye on several kinds of semiconductors are also shown in Table 1. The absorption peaks of the dye on Nb_2O_5 and TiO_2 were almost the same at 545 nm and red-shifted compared to that of the dye in the ethanol solution (534 nm). The red shift was observed in most films, while a significant blue shift was observed in ZnO. The TiO_2 red shift is explained by the strong interaction between the dye and cationic semiconductor surface and by the delocalized π^* state of the Ru−complex ligand into the TiO_2 conduction band.[2] It is considered that the strong interaction between the Ru dye and the Nb_2O_5 surface is present, as is the case for TiO_2. Redmond et al. attributed the blue shift in the case of ZnO to a change of semiconductor−electrolyte solution interface, aggregation of dye molecules, or dye chemisorption onto specific sites of the ZnO surface.[3] The absorption spectrum of the $(NCS)_2RuL_2$ dye is known to shift to a shorter wavelength at a higher pH.[10] ZnO is often classified as a basic oxide due to the strong basic sites on the surface, while others are generally acidic oxides. We thus speculate that the basicity of ZnO surface sites is the main reason for the blue shift.

The binding state between the $(NCS)_2RuL_2$ dye and semiconductor was studied using FTIR spectroscopy, as shown in Figure 5. The Ru dye spectra on several kinds of semiconductors differed greatly. The absorption at about 2000 and 2100 cm^{-1} is attributed to the SCN ligand stretching modes.[10] The absorption peak at about 1730 cm^{-1} is assigned to the carboxyl group C=O stretching band, which contributes to the formation of an ester-like linkage between the dye molecules and the semiconductor surface, and absorption at about 1605 cm^{-1} is assigned to the carboxyl group O−C−O asymmetrical stretching, which contributes to the interaction through chelating or bridging modes to the semiconductor surface.[10−12] Strong absorption of the ester-like linkage on the Nb_2O_5 semiconductor(a) was observed at 1733 cm^{-1}, while the chelating absorption at about 1605 cm^{-1} was small. In the case of TiO_2 (b), ZrO_2 (c), and

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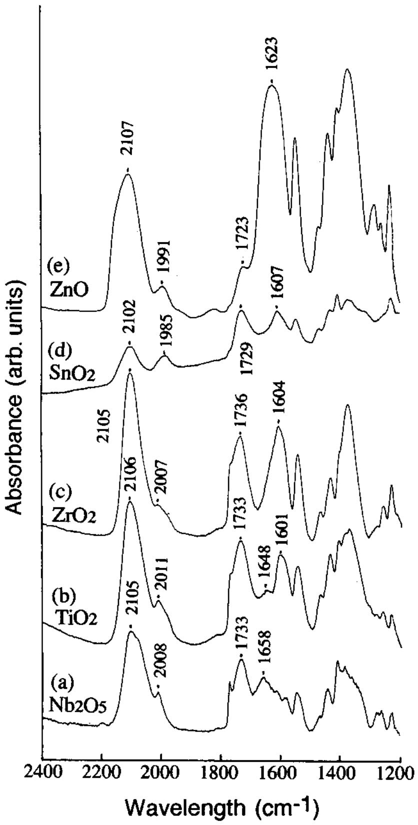

Figure 5. FTIR spectra in diffuse reflectance mode of the $(NCS)_2RuL_2$ dye on several types of semiconductors.

SnO_2, (d), both an ester-like linkage and chelating linkages were observed. The dye spectra on Ta_2O_5, WO_3, and In_2O_3 could not be measured because the amount of adsorbed dye was so low. On the other hand, the spectrum of ZnO (e) was very different from the others. Strong absorption was observed at 1623 cm^{-1}, possibly contributing to the strong chelating interaction between the Ru dye and special ZnO surface sites such as basic sites, because strong interaction changes the O−C−O angle and shifts the absorption.[12]

Regarding the relationship between electron-transfer efficiency and the condition of the Ru dye linkage to the semiconductor surface, Murakoshi et al. reported[10] that an increase in the ratio of ester-like linkage to chelating linkage was related to an increase of the photocurrent in the $(NCS)RuL_2$ dye/TiO_2 cell. Moreover, Goodenough et al. stated that the electron injection from the RuL-$(bipy)_2$ sensitizer to the conduction band of the TiO_2 single-crystal was more effective than that of SnO_2 because the $RuL(bipy)_2$ dye adhered to semiconductor surfaces through an ester linkage and electrons were transferred mainly through the conjugated orbitals of the ester linkage and the semiconductor conduction band.[13] The TiO_2 conduction band consists of Ti_{3d} and that of SnO_2 consists of a Sn_{5s} orbital. The orbital overlap between the conduction band and the ester linkage suggests that electron transfer from the Ru dye to the semiconductor d-orbital is more effective than that from the Ru dye to the s-orbital due to the orbital shape. It is very important whether electron transfer from a dye to a semiconductor takes place through a conjugated linkage or not. For SnO_2 electrodes sensitized by perylene derivatives, the dye with a conjugated linkage was more efficient than that with a nonconjugated linkage.[14] On the other hand, some reports have stated that the electrons of the Ru complex can transfer to the TiO_2 conduction band through space and that a conjugated linkage was not essential for such transfer.[15,16] However, the IPCE of the cell that had an intimate electronic coupling between the TiO_2 surface link and the chromophoric ligand was higher than that without.[15] From the discussions mentioned above, we surmised that electron-transfer took place both through space and a conjugated linkage, but the route through the conjugated linkage was more advantageous than that through space. Therefore, the situation of the linkage between the dye and the semiconductor is a very important factor in determining the photocurrent efficiency. In our present study, the conduction bands of TiO_2, Nb_2O_5, Ta_2O_5, WO_3, and ZrO_2 consist of d-orbitals, and those of ZnO, SnO_2 and In_2O_3 consist of s-orbitals, meaning that the best two semiconductors for photocurrent belong to the d-orbital group. According to Goodenough,[13] the semiconductor conduction band being d-orbitals may be one of the most important factors for increasing electron injection efficiency for dyes having an anchor group as an electron pathway.

Photocurrent efficiency may also be influenced, however, by not only the linkage situation but also many other factors such as the amount of adsorbed dye, the photoconductivity of the semiconductor, the electrical contact between particles, the electron back-transfer, the location of the conduction band potential, and the dye redox potential in the ground state and excited state. ZrO_2 and Ta_2O_5 cells showed poor efficiency because of the highly negative conduction band potential and low surface area, mentioned above. At least in our results, the difference between the s- and d-orbitals of the conduction band explains why the TiO_2 and Nb_2O_5 cells showed a higher efficiency than other semiconductor cells, while the other factors cannot explain our results clearly.

3. Nb_2O_5 Film Electrode Treatments To Improve Cell Efficiency. The efficiency of the TiO_2 cell sensitized by the $(NCS)_2RuL_2$ dye is known to be improved by $TiCl_4$ treatment of TiO_2 film.[2] To increase the efficiency of the Nb_2O_5 cell, we studied several types of treatment, as shown in Table 3. All porous Nb_2O_5 film electrodes were made of Nb_2O_5 powder prepared from $Nb(OH)_5$ at 700 °C for 1 h in air. It was found that the photocurrent of the dye-sensitized Nb_2O_5 cell was slightly improved by $NbCl_5$ ethanol solution treatment and that it was significantly improved by niobium alkoxide solution treatments, in which the solution was dropped on the Nb_2O_5 film electrode and then was calcined again at 500 °C before dye adsorption. Photocurrent−voltage curves of dye-sensitized Nb_2O_5 cells with and without $Nb(OC_2H_5)_5$ treatment are shown in Figure 6. Both photocurrent and fill factor were im-

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Table 3. Effect of Several Types of Nb_2O_5 Film Treatment before $(NCS)_2RuL_2$ Dye Adsorption upon Photoelectrochemical Properties of Nb_2O_5 Cells[a]

treatment	V_{oc}, V	I_{sc}, mA	fill factor, %	IPCE, %
no treatment	0.60	0.31	63	19
$Nb(OC_2H_5)_5$ (0.2 mol/L in ethanol)[b]	0.58	0.48	80	29
$Nb(OC_4H_9)_5$ (0.2 mol/L in butanol)[b]	0.57	0.44	79	26
$NbCl_5$ saturated solution in ethanol [c]	0.58	0.35	65	21

[a] Porous Nb_2O_5 films were made of Nb_2O_5 powder prepared from $Nb(OH)_5$ (Central Glass) at 700 °C for 1 h in air. Film thickness = 6−8 μm. Dye sensitizer, $(NCS)_2RuL_2$. Solar cell properties were measured for monochromatic light through a band-pass filter (520 nm, 4 mW/cm^2). Semiconductor film electrode area = 1 × 1 cm. Irradiation area = 1 × 1 cm. [b] Niobium alkoxide solution was dropped on the untreated Nb_2O_5 film electrode and dried at room temperature. After coating was repeated 10 times, the electrode was fired again at 500 °C in air. [c] The Nb_2O_5 film electrode was soaked in $NbCl_5$-saturated solution for 96 h, dried, and fired again at 500 °C in air.

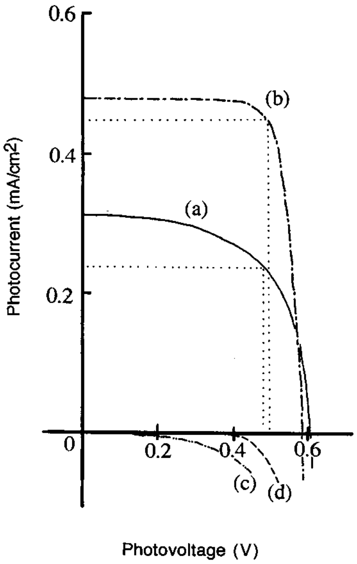

Figure 6. Photocurrent−voltage curves of the dye-sensitized Nb_2O_5 cell with or without $Nb(OC_2H_5)_5$ treatment under monochromatic light through a 520 nm band-pass filter (4 mW/cm^2). (a) Photocurrent and (c) dark current of the untreated $(NCS)_2RuL_2/Nb_2O_5$ cell. (b) Photocurrent and (d) dark current with $Nb(OC_2H_5)_5$ treatment. The electrolyte solution was 0.5 mol/L tetra-*n*-propylammonium iodide and 0.05 mol/L iodine in ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume).

proved, and the dark current was shifted to a more positive voltage by the treatment. Figures 7 and 8 shows SEM photographs of Nb_2O_5 film electrode with and without $Nb(OC_2H_5)_5$ treatment. The porous nature of these films is clear, and particles are mainly between 100 and 200 nm in both electrodes. The particle surfaces became rough and many particles were agglutinated after treatment. This treatment increased the amount of dye adsorbed on the Nb_2O_5 surface 1.2 times. In the case of the $TiCl_4$ treatment of the TiO_2 electrode, the deposition of a pure TiO_2 layer on TiO_2 particles was speculated to yield a high efficiency.[2] We used highly pure $Nb(OC_2H_5)_5$ (99.999%) in this study. It was considered that the effects of the niobium alkoxide treatment were attributed to several factors: the increase of dye adsorbed on the electrode, good

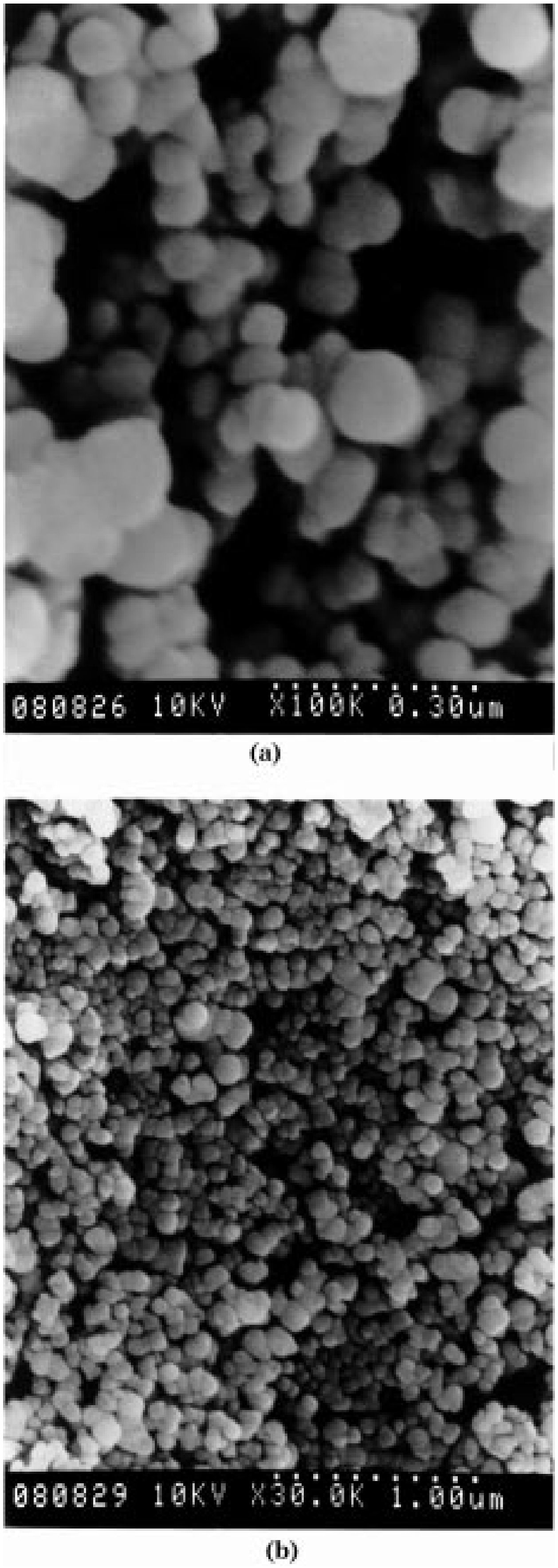

Figure 7. SEM photographs of Nb_2O_5 film on conducting glass before $Nb(OC_2H_5)_5$ treatment: (a) high and (b) low magnification of the Nb_2O_5 film. The film was made of powder precalcined at 700 °C for 1 h.

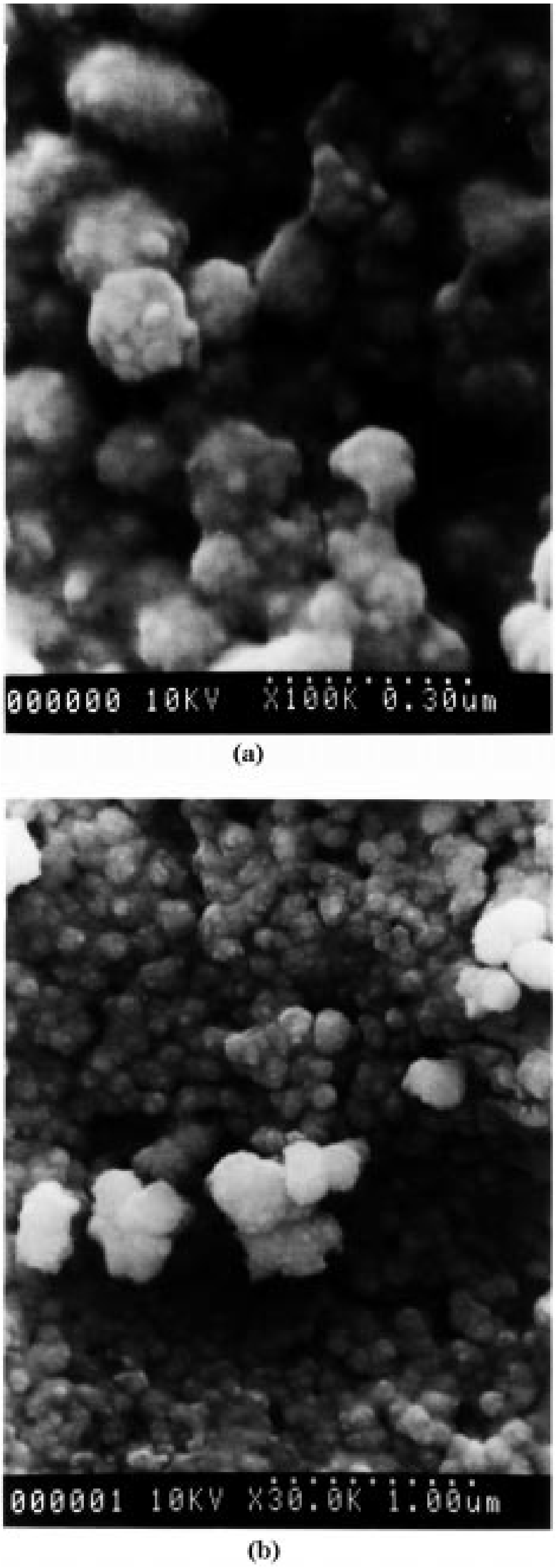

Figure 8. SEM photographs of Nb_2O_5 film on conducting glass precalcined at 700 °C after $Nb(OC_2H_5)_5$ treatment. $Nb(OC_2H_5)_5$ solution was dropped on the nontreated Nb2O5 film (Figure 7), and dried at room temperature. After coating was repeated 10 times, the electrode was fired in air at 500 °C for 1 h.

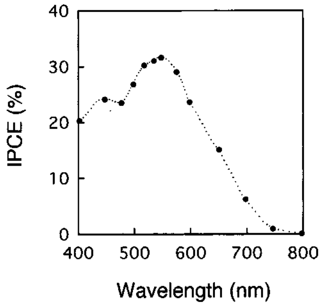

Figure 9. Photocurrent action spectrum for the dye-sensitized Nb_2O_5 cell with $Nb(OC_2H_5)_5$ treatment. The spectrum was obtained using a thin-layer cell (1 × 1 cm) containing 0.5 mol/L tetra-*n*-propylammonium iodide and 0.05 mol/L iodine in ethylene carbonate and dry acetonitrile mixed solvent (60:40 by volume) under monochromatic light passed through a band-pass filter (3−5 mW/cm^2).

photoconductivity between Nb_2O_5 particles, and the deposition of a highly pure Nb_2O_5 layer on the porous Nb_2O_5 electrode. Figure 9 shows the photocurrent action spectrum for the dye-sensitized Nb_2O_5 cell with $Nb(OC_2H_5)_5$ treatment. The maximum IPCE using a 548 nm band-pass filter was estimated at 32%, and the shape of the action spectrum was similar to that of the UV−vis spectrum of $(NCS)_2RuL_2/Nb_2O_5$ (Figure 4d). Measurement for the overall energy-to-electric energy conversion efficiency was also performed using a solar simulator, and about 2% efficiency (I_{sc} = 4.9 mA/cm^2, V_{oc} = 0.63 V, fill factor = 0.66, illumination area = 0.5 cm^2, 100 mW/cm^2) was obtained. This overall efficiency was as same as the best value for the ZnO cell thus far,[4] but smaller than that for the TiO_2 cell. The short circuit photocurrent of the TiO_2 cell was improved by various kinds of treatments and modifications, such as $TiCl_4$ treatment, yielding >80% IPCE.[2] In the ZnO cell, the IPCE in an early report[3] was only <13%, but it improved to 58% by modifying the ZnO preparation.[4] The photocurrent is easily influenced by various kinds of factors, and we anticipate that the Nb_2O_5 cell IPCE will become as good as that of the TiO_2 cell by finely tuned optimization, which will directly lead to an excellent overall energy conversion efficiency. We conclude that Nb_2O_5 is potentially a good candidate as a porous semiconductor electrode for dye-sensitized solar cells. The high photovoltage of the Nb_2O_5 cell is attractive as a power source for electrical appliances such as watches and calculators. These electrical appliances do not require much current but need a minimum level of voltage, e.g., >1.8 V for the typical calculator. This requires that solar cells must be connected in series. The high working voltage of the solar cell leads to a decrease in the number of cell connections and to a decrease in the manufacturing cost. Moreover, the Nb_2O_5 semiconductor has the advantage of photocatalytic activity that is very low compared to TiO_2 under UV light.[17] Photocatalytic decomposition of dye and organic solvents over the semiconductor itself is a serious problem under solar UV light, because even a slight gas evolution by photocatalysis may destroy the sealed cell.

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Conclusions

We prepared a variety of porous semiconductor electrodes, TiO_2, Nb_2O_5, ZnO, SnO_2, In_2O_3, WO_3, Ta_2O_5, and ZrO_2, from several oxide powders and their precursors and measured the photoelectrochemical properties of electrodes sensitized by the ruthenium(II) *cis*-bis(thiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) complex. We drew the following conclusions from the results of this study:

(1) The TiO_2 semiconductor cell showed the highest short-circuit photocurrent (I_{sc}), and the Nb_2O_5 cell prepared from $Nb(OH)_5$ showed the next highest I_{sc}, compared to the TiO_2 cell. The fill factor of the Nb_2O_5 cell was as good as that of the TiO_2 cell and was much higher than those of other cells. The open-circuit photovoltage (V_{oc}) of the Nb_2O_5 cell was the highest in all semiconductor cells, and the TiO_2 cell V_{oc} was the next highest. The photon-to-electric energy conversion efficiency of the TiO_2 and Nb_2O_5 cells was thus much higher than those of other semiconductor cells.

(2) Ru dye adhered to the Nb_2O_5 and TiO_2 surface mainly through an ester-like linkage. It is speculated that electrons transfer mainly through the conjugated orbitals of the ester linkage and semiconductor conduction band. The orbital overlap between the conduction band and ester linkage suggests that electron transfer from the Ru dye to the semiconductor d-orbital is more effective than that from the Ru dye to the s-orbital due to orbital shape. We thus considered that a TiO_2 and Nb_2O_5 conduction band consisting of d-orbitals was more advantageous than that of s-orbitals for efficient IPCE.

(3) The photoelectrochemical properties of the Nb_2O_5 electrode sensitized by Ru dye were influenced by several factors. A higher precalcination temperature and thinner Nb_2O_5 film thickness were suitable for the higher open-circuit cell photovoltage of the Nb_2O_5 cell. For the highest photocurrent, the 8 μm thickness of the Nb_2O_5 film prepared from powder precalcined at 700 °C was the most suitable. The cell efficiency was markedly improved by treating the Nb_2O_5 electrode with Nb alkoxide. The maximum IPCE reached 32% at 548 nm. The overall solar-to-electric energy conversion efficiency was about 2% (AM-1.5, 100 mW/cm^2).

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