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TiO_{2-x} 박막의 광-전기화학적 성질에 관한 연구

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Studies on the Photo-electrochemical Properties of TiO_{2-x} Thin Films

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요 약. 티타늄 금속판을 수증기 산화하여 만든 TiO_{2-x} 박막과 TiO_2 단결정을 알곤기체속에서 환원한 시료를 사용하여 이들의 광전기화학적 성질을 연구하였다. 1*M* NaOH 전해질 용액에서 TiO_{2-x} 전극에 200~800nm 사이의 광을 조사하였을 때 자외부 영역에서는 320nm 에서, 가시부 영역에서는 520nm, 620nm 그리고 740nm 에서 전류의 peak 가 나타났다. 이미 보고된 것과는 대조적으로 가시부 영역의 이들 peak 는 grating monochromator 의 2 차선의 영향에 의하여 나타난 것임이 밝혀졌다.

ABSTRACT. The thin films of TiO_{2-x} were prepared by vapor oxidation and TiO_2 single crystal was reduced by heating in argon atmosphere. The photo-electrochemical properties of these samples were studied. When the photocurrent was scanned in 1*M* NaOH electrolyte solution, several peaks were observed in the vicinity of 320nm in the UV-region and in the vicinity of 520nm, 620nm, and 740nm in the visible-region. Contrary to the previous supositions, those peaks were produced by the second-order lines from the grating monochromator.

I. INTRODUCTION

Since Fujishima and Honda[1] first observed the photoelectrolysis of water with reduced single crystal TiO_2, the photovoltaic behavior of *n*-type TiO_2 electrodes of both single and polycrystalline forms have been studied extensively.[2,3] Since the energy band gap of semiconduction titanium dioxide is about 3 eV, the photoresponse is expected to be centered around 320nm.

The present work is concerned with the nature of the photoresponse of the TiO_{2-x} thin film prepared by water vapor oxidation and TiO_2 single crystal reduced by heating in gattered argon gas.

When the TiO_{2-x} electrodes were irradiated, an electric current was generated. When the photocurrent was scanned, several peaks were observed in the vicinity of 320nm in the UV-region and in the vicinity of 520nm, 620nm, and 740nm in the visible-region.

To determine whether these peaks that appeared in the visible-region are caused by the first order radiation of the grating monochromator, the photocurrents were studied by using various filters.

II. EXPERIMENTAL

1. Materials Preparation[4]

Titanium sheets ($1\times1\times0.1cm^3$) used were 5-*N* purity titanium. Titanium sheets were polished with automatic crystal polisher(Model DS-701G, Jasco) by using alumina powder of 0.2 μm size, etched in CP_4 (mixed solution of HNO_3;50m*l*, glacial acetic acid; 30m*l*, HF; 30 m*l*, Br_2;1 drop) for one minute, rinsed with the double distilled water and then with distilled isopropyl alcohol, and dried in vacuum oven for one hour at 50°C.

The TiO_{2-x} thin films were grown by passing water saturated argon gas(50m*l*/min) over the titanium sheets in the electrical furnace at temperature 800°C, 900°C, 1140°C respectively, for thirty minuties.[5,6]

2. Transmission Characteristics of Various Filter Used.

[1] Solution used for filters

(1) 1.0*M* $CuSO_4$ solution, 250g/*l*; to dissolve extra pure reagent $CuSO_4$ $5H_2O$ in distillated water.

(2) 0.85*M* $CoSO_4$ solution, 240g/*l*; to dissolve extra pure reagent $CoSO_4$ $7H_2O$ in distillated water.

(3) 0.018*M* anthracene solution, 10g/*l*; to dissolve extra pure reagent anthracene in cyclohexane.

(4) 1.14*M* $TiCl_4$ solution[11]; to dissolve $TiCl_4$ 50m*l* in 6*M* HCl 150m*l*

These solutions were kept in the acrylic cell with the quartz windows ($1\times1\times0.1cm^3$) on both side.

[2]. Solid filters

(1). TiO_2 single crystal filter; a single crystal (Commercial crystal Labs. InC.) of 1mm thickness was polished with automatic crystal polisher(Model DS 701G Jasco), using alumina powder of 0.2μm size.

(2). UV filter; Corning number 7-51.

(3). Glass filter; glass of 2mm thickness.

[3]. Measurement of transmissions for various filters

Light transmissions for various filters in 1cm path length-quartz cells were measured with UV-Vis spectrophotometer(Super Scan III Varian). These results are shown in *Fig.* 2~8.

3. Measurements of Photocurrent

The photocurrents of TiO_{2-x} electrodes in 1*M* NaOH solution were measured with air bubbling by using convensional three electrodes, in which the TiO_{2-x} was the working electrode, the saturated calomel electrode (SCE) the reference electrode, and the platinum electrode ($2\times2cm^2$) the counter electrode. The elec-

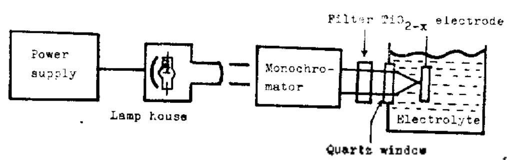

Fig. 1. Schematic diagram for photocurrent measurement.

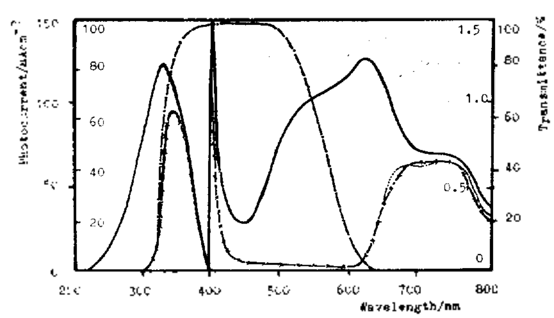

Fig. 2. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·-; Transmittance of $CuSO_4$ (1.0*M*) solution, ———; Photocurrent without filter, -×-×-×-; Photocurrent with filter, ············; Calculated curve of $T_0P_2/100$.

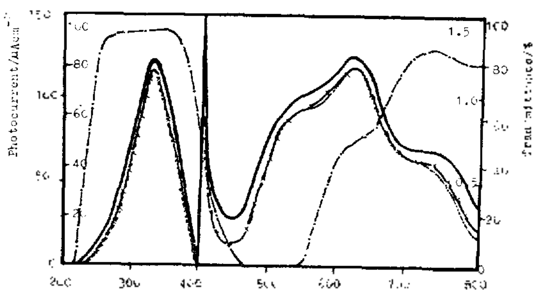

Fig. 3. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. —·—·; Transmittance of $CoSO_4$(0.85*M*) solution, ————; Photocurrent without filter, -×-×-×; Photocurrent with filter, ············; Calculated curve of $T_0P_2/100$.

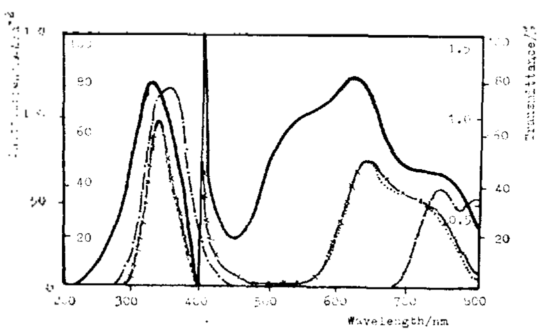

Fig. 4. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·-·; Transmittance of 7-51 UV filter, ————; Photocurrent without filter, -×-×-×-; Photocurrent with filter, ············; Calculated curve of $T_0P_2/100$.

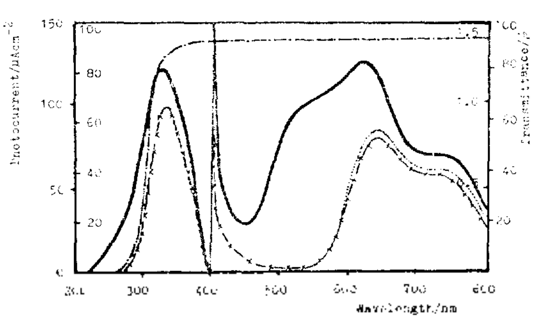

Fig. 5. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·; Transmittance of glass filter, ————; Photocurrent without filter, -×-×-×-×; Photocurrent with filter, ············; Calculated curve of $T_0P_2/100$.

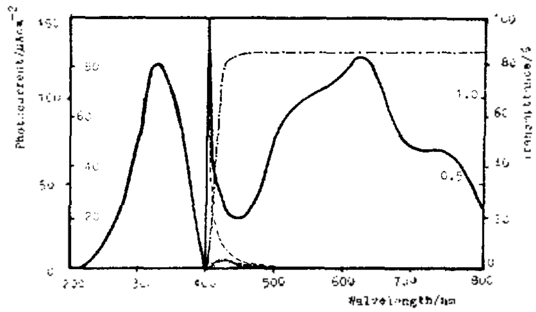

Fig. 6. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·; Transmittance of anthracene (0.018*M*) solution, ————; Photocurrent without filter, -×-×-×; Photocurrent with filter, ············; Calculated curve of $T_0P_2/100$.

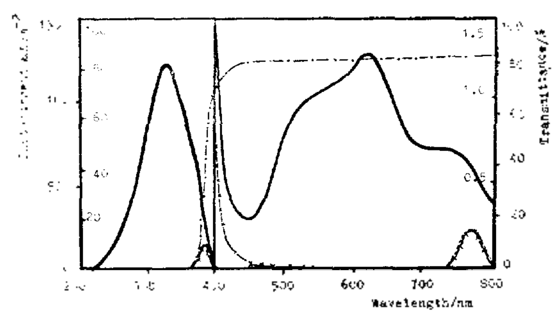

Fig. 7. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·; Transmittance of TiO_2 single crystal filter, ————; Photocurrent without filter, -×-×-×; Photocurrent with filter, ············; Calculated curve of $P_3T_1\times100$.

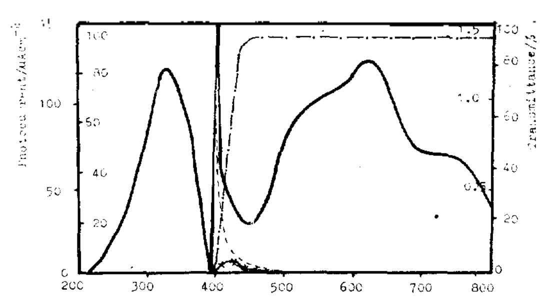

Fig. 8. Photoresponses of 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution at OV vs. SCE. -·-·-·; Transmittance of $TiCl_4$ (1.14*M*) solution, ———— ;Photocurrent without filter, -×-×-×; Photocurrent with filter, ············; Calculated curve of $P_3/T_1\times100$.

trode potential was controlled by using the potentiometer of the potentiostat prepared in our Lab.[7]

The quartz window was placed at a distance of 1.4cm from the high-intensity monochromator (Bausch and Lomb 1350 Groves/mm, 300nm Blaze, entrance slit;5.36mm, exit slit;3.00mm). The lamp (150W Xe-lamp oriel 8500, current; 7.5A, voltage;DC 20V) was housed in Oriel universal lamp housing (Baush and Lomb cat. No. 33-86-75).

The TiO_{2-x} electrodes were positioned 2.4cm from the exit slit of the monochromator; the distance between TiO_{2-x} electrode and quartz window of the cell was 1cm. The electrical circuit and optical arrangement are schematically shown in *Fig.* 1. The photocurrents of TiO_{2-x} electrodes were measured at wavelength region 200~800nm (17nm/min) with various filters in 1*M* NaOH electrolyte solution, and recorded in the Y-axis of the X-Y recorder. These results are shown in *Fig.* 2~8.

III. RESULTS AND DISCUSSION

(1) When the TiO_{2-x} electrode was irradiated, the electric current was generated. When the photocurrent was scanned, several peaks were observed in the vicinity of 320nm in the UV-region and in the vicinity of 520nm, 620nm, and 740nm in the visible-region as shown in *Fig.* 2~8 and summarized in *Table* 1.

To determine whether these three peaks that appeared in the visible-region are caused by the first order radiation of the visible-region or the second order radiation of the grating monochromator, the photocurrents were studied by using various filters and the following results as shown in *Fig.* 2~8. were obtained.

(1). Only one photocurrent peak was observed in the vicinity of 740nm when a filter was filled with 1.00*M* $CuSO_4$ solution (*Fig.* 2).

(2). Three photocurrent peaks were observed in the vicinity of 520nm, 620nm, and 740nm when a filter was filled with 0.85*M* $CoSO_4$ solution (*Fig.* 3).

(3). Two photocurrent peaks were observed in the vicinity of 620nm, and 740nm when a 7-51 UV filter or glass filter was used (*Fig.* 4, 5).

(4). Only one photocurrent peak was observed in the vicinity of 780nm when a filter filled with 0.018*M* anthracene solution (*Fig.* 6).

(5). When the TiO_2 single crystal or 1.14*M* $TiCl_4$ solution was used as the filter which block the UV radiation entirely, the photocurrent gradually decreased and it was negligible

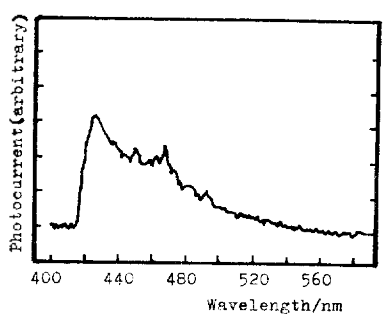

Fig. 9. Photoresponses of a TiO_2 sample in 1*M* KOH solution at OV vs. SCE by Butler and Decker.

Table 1. Peaks of photocurrent of TiO_{2-x} electrodes in 1*M* NaOH solution

S.C.		800(VO)		900(VO)		1140(VO)	
nm	$\mu A/cm^2$	nm	$\mu A/cm^2$	nm	$\mu A/cm^2$	nm	$\mu A/cm^2$
331	127	323	116.8	321	80	324	123.5
518	0.98	528	0.750	525	0.725	525	0.935
613	1.28	625	0.800	621	0.812	620	1.262
753	0.28	753	0.502	753	0.650	745	0.711

Table 2. The values of photocurrent for 1140(VO) TiO_{2-x} electrode according to transmittance of the $CuSO_4$ solution filter and relative errors

Wavelength/nm	T_0/%	$P_0/\mu A$	$P_1/\mu A$	$\frac{T_0P_0}{100}$ ($P_1'/\mu A$)	$\frac{P_1-P_1'}{P_1'}\times 100$ (%)	Wavelength/nm	$P_2/\mu A$	$P_3/\mu A$	$\frac{T_0P_2}{100}$ ($P_3'/\mu A$)	$\frac{P_3-P_3'}{P_3'}\times 100$ (%)
305	0.0	94.0	—	0.0	0.0	610	1.250	0.012	0.0	—
310	4.5	103.1	4.6	4.6	0.0	620	1.270	0.090	0.057	57.9
315	8.5	112.5	9.6	9.6	0.0	630	1.234	0.159	0.130	22.3
320	23.5	123.2	28.5	29.0	−1.7	640	1.160	0.281	0.272	3.3
325	43.4	123.5	53.0	53.6	−1.1	650	1.041	0.420	0.450	−6.7
330	60.6	121.5	72.8	73.6	−1.1	660	0.932	0.512	0.560	−8.6
335	72.8	117.0	85.0	85.2	−0.2	670	0.860	0.611	0.611	0.0
340	80.7	110.5	88.2	89.2	−1.1	680	0.776	0.624	0.625	−0.2
345	86.2	103.2	87.5	89.0	−1.7	690	0.720	0.640	0.630	1.6
350	90.2	95.5	85.4	86.1	−0.8	700	0.750	0.642	0.631	1.7
355	92.0	87.0	79.2	80.0	−1.0	710	0.694	0.649	0.635	2.2
360	93.7	79.5	73.0	74.5	−0.8	720	0.695	0.652	0.642	1.6
365	95.2	70.5	66.3	67.1	−1.2	730	0.701	0.655	0.651	0.6
370	96.0	61.5	58.6	59.0	−0.7	740	0.705	0.653	0.652	0.2
375	96.8	52.0	49.9	50.3	−0.8	750	0.693	0.645	0.653	−1.2
380	97.2	41.5	40.0	40.3	−0.7	760	0.660	0.615	0.630	−2.4
385	97.7	30.5	29.4	29.8	−1.3	770	0.595	0.553	0.571	−3.2
390	97.9	6.8	6.6	6.7	−1.5	780	0.526	0.451	0.500	−9.8
395	98.3	3.4	3.4	3.3	3.0	790	0.450	0.383	0.442	−13.4
400	98.4	1.5	1.4	1.4	0.0	800	0.385	0.274	0.378	−27.5

Table 3. The values of photocurrent for 1140(VO) TiO_{2-x} electrode according to transmittance of the $CoSO_4$ solution filter and relative errors

Wavelength/nm	T_0/%	$P_0/\mu A$	$P_1/\mu A$	$\frac{T_0P_0}{100}$ ($P_1'/\mu A$)	$\frac{P_1-P_1'}{P_1'}\times 100$ (%)	Wavelength/nm	$P_2/\mu A$	$P_3/\mu A$	$\frac{T_0P_2}{100}$ ($P_3'/\mu A$)	$\frac{P_3-P_3'}{P_3'}\times 100$ (%)
240	72.0	8.2	5.8	5.9	−1.7	480	0.531	0.392	0.383	2.4
250	88.0	13.6	12.1	12.0	0.8	500	0.780	0.689	0.686	0.4
260	90.0	20.4	18.5	18.4	0.5	520	0.941	0.849	0.947	0.3
270	91.0	29.5	26.8	26.9	−0.3	540	1.005	0.917	0.915	0.2
280	92.0	43.6	40.2	40.1	0.3	560	1.035	0.955	0.952	0.3
290	92.5	61.8	56.3	56.2	0.2	580	1.093	1.032	1.011	2.1
300	93.0	83.0	77.3	77.2	0.1	600	1.190	1.110	1.107	0.3
310	93.2	103.1	96.2	96.1	0.1	620	1.270	1.180	1.184	−0.3
320	93.5	123.2	115.1	115.2	−0.1	640	1.160	1.110	1.085	2.3
330	93.8	121.5	114.2	114.0	0.2	660	0.932	0.873	0.874	−0.1
340	93.9	110.5	103.4	103.8	−0.4	680	0.776	0.733	0.729	0.5
350	93.8	95.5	89.1	89.6	−0.6	700	0.705	0.664	0.661	0.5
360	89.6	79.5	71.3	71.2	0.1	720	0.695	0.627	0.623	0.6
370	84.0	61.5	51.4	51.7	−0.6	740	0.705	0.601	0.592	1.5
380	77.0	41.5	29.4	32.0	−8.1	760	0.660	0.518	0.508	2.0
390	63.0	6.8	4.4	4.3	2.3	780	0.526	0.350	0.331	5.7
400	50.0	1.5	0.8	0.8	0.0	800	0.385	0.210	0.193	8.8

Table 4. The values of photocurrent for 1140(VO) TiO_{2-x} electrode according to transmittance of the 7-51 UV filter and relative errors

Wavelength/nm	$T_0/\%$	$P_0/\mu A$	$P_1/\mu A$	$\frac{T_0P_0}{100}$ $(P_1/\mu A)$	$\frac{P_1-P_1}{P_1}\times 100$ (%)	Wavelength/nm	$P_2/\mu A$	$P_3/\mu A$	$\frac{T_0P_2}{100}$ $(P_3'/\mu A)$	$\frac{P_3-P_3'}{P_3'}\times 100$ (%)
290	11.6	61.8	7.1	7.2	−1.4	580	1.093	0.140	0.127	10.2
300	31.0	83.0	25.5	25.7	−0.8	600	1.190	0.390	0.396	7.1
310	46.4	103.1	47.4	47.8	−0.8	620	1.270	0.645	0.589	9.5
320	67.5	123.2	82.1	83.2	−1.3	640	1.160	0.785	0.783	0.3
330	71.5	121.5	86.2	86.9	−0.8	660	0.932	0.718	0.666	7.8
340	76.8	110.5	84.9	84.9	0.0	680	0.776	0.625	0.600	4.2
350	80.0	95.5	75.8	76.4	−0.8	700	0.705	0.581	0.564	3.0
360	77.5	79.56	1.2	61.6	−0.7	720	0.695	0.545	0.539	1.1
370	70.0	61.5	42.1	43.1	−4.4	740	0.705	0.496	0.494	0.4
380	55.5	41.5	23.2	23.0	0.9	760	0.660	0.390	0.366	6.6
390	43.0	6.8	3.0	2.9	3.5	780	0.526	0.250	0.226	10.6
400	20.0	1.5	0.3	0.3	0.0	800	0.385	0.100	0.077	29.9

P_1, P_3; Photocurrent with filter, P_0, P_2; Photocurrent without filter, T_0; Transmittance of filter.

Table 5. The values of photocurrent for 1140(VO) TiO_{2-x} electrode according to transmittance of the glass filter and relative errors

Wavelength/nm	$T_0/\%$	$P_0/\mu A$	$P_1/\mu A$	$\frac{T_0P_0}{100}$ $(P_1'/\mu A)$	$\frac{P_1-P_1'}{P_1'}\times 100$ (%)	Wavelength/nm	$P_2/\mu A$	$P_3/\mu A$	$\frac{T_0P_2}{100}$ $(P_3'/\mu A)$	$\frac{P_3-P_3'}{P_3'}\times 100$ (%)
275	3.5	36.0	1.34	1.26	6.3	550	1.015	0.044	0.036	22.2
290	20.0	61.8	13.0	12.4	4.8	580	1.093	0.195	0.219	−10.0
300	42.0	83.0	35.5	40.5	−12.3	600	1.190	0.391	0.440	−11.8
310	59.0	103.1	61.0	60.8	0.3	620	1.270	0.643	0.685	−8.5
320	80.0	123.2	89.0	98.5	−9.6	640	1.134	0.773	0.817	−9.6
325	82.0	123.5	98.5	110.3	−2.8	650	1.041	0.759	0.805	−5.7
335	88.1	117.0	99.5	103.0	−3.4	670	0.860	0.657	0.706	−6.7
350	90.0	95.5	85.2	85.9	−0.8	700	0.705	0.578	0.607	−4.3
370	90.1	60.5	50.2	54.4	−7.7	740	0.690	0.551	0.588	−5.3
390	90.2	6.8	6.1	6.0	−1.7	780	0.560	0.385	0.418	−17.0
400	90.2	1.5	1.4	1.3	−7.7	800	0.385	0.255	0.282	−18.5

P_1, P_3; Photocurrent with filter, P_0, P_2; Photocurrent without filter, T_0; Transmittance of filter.

around 600nm and the three peaks did not appear (*Fig*. 7, 8). The pattern of variation of the photocurrent with wavelength was agreed with that reported by Butler and Decker[8] except for the small spikes as shown in *Fig*. 9.

[2] Since the filters used had non zero transmittance with various wavelength, the observed photocurrents with filters were converted to 100% transmittance.

Namely, $\frac{P_0T_0}{100}$ and $\frac{P_2T_0}{100}$ were computed for the observed photocurrent without filter and compared with the observed photocurrent when the filter was used. The computed values of $\frac{P_0T_0}{100}$ and $\frac{P_2T_0}{100}$ agreed with the P_1, P_3 at each wavelength, with relative deviation less than 3% and 5% respectively as shown in *Fig*. 2∼5

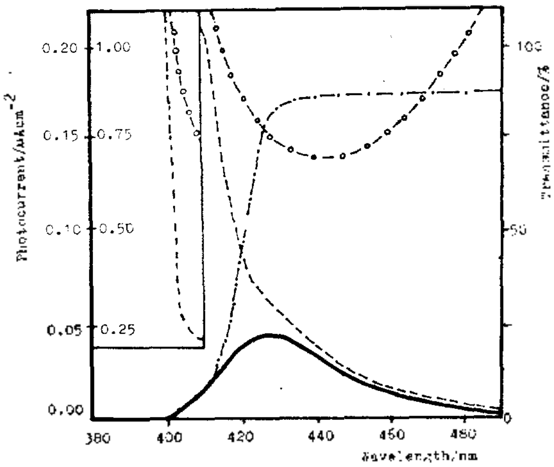

Fig. 10. Relation of photocurrent and transmittance of TiO_2 single crystal filter for 1140(VO) in 1*M* NaOH. -○-○-; Photocurrent without filter, ———; Photocurrent with filter, -·-·-·; Transmittance of filter, -------; $\frac{\text{Photocurrent}}{\text{Transmittance}}\times 100$.

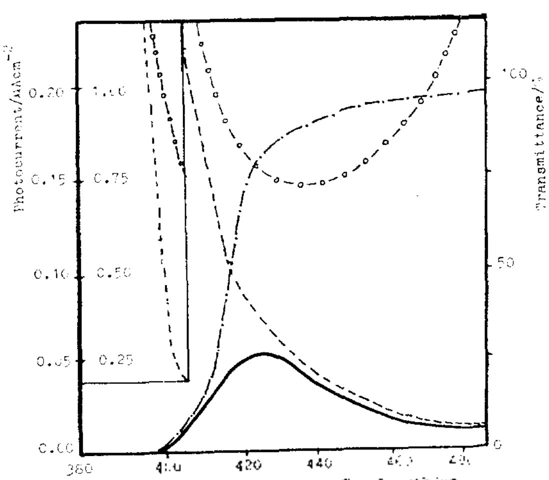

Fig. 11. Relation of photocurrent and transmittance of $TiCl_4$ (1.14*M*) filter for 1140(VO) in 1*M* NaOH solution. -○-○-; Photocurrent without filter, ———; Photocurrent with filter, -·-·-·-; Transmittance of filter, -------; $\frac{\text{Photocurrent}}{\text{Transmittance}}\times 100$.

and were summarized in *Table* 2~5.

Where T_0; the transmittance of filters in the UV-region or the transmittance of filters in the UV-region corresponding to $\frac{1}{2}$ wavelength of the visible region.

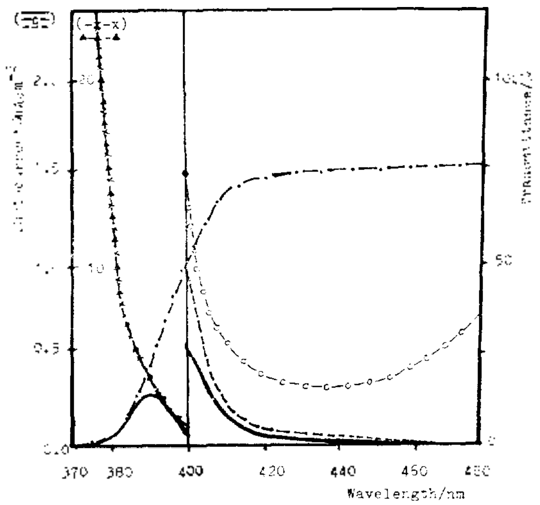

Fig. 12. Relation of photocurrent and transmittance of anthracene (0.018*M*) filter for 1140(VO) in 1*M* NaOH solution. -○-○-, -▲-▲-▲; Photocurrent without filter, ———; photcurrent with filter, -·-·-·-; Transmittance of filter, ················, ×-×-×-×; $\frac{\text{Photocurrent}}{\text{Transmittance}}\times 100$.

P_0; the photocurrent obtained without filter in the UV-region.

P_1; the photocurrent obtained with filter in the UV-region.

P_2; the photocurrent obtained without filter in the visible-region.

P_3; the photocurrent obtained with filter in the visible-region.

The photocurrents of the visible region using TiO_2 single crystal and $TiCl_4$ solution filters were observed to have the values of maximum in near 430nm as shown in the solid line of *Fig.* 10, 11.

These peak currents were supposed to be the consequence of variations of the transmittance of the filters in the visible region.

In consideration of the transmittance of filters, the computed values of $\frac{P_3}{T_1}\times 100$ were given the same values for the various filters at each wavelength of the visible region as shown

Table 6. The values of photocurrent according to transmittance of the filters for 1140(VO) TiO_{2-x} electrode in 1*M* NaOH

Filter / nm	TiO_2 single crystal			Anthracene solution			$TiCl_4$ solution		
	$T_1/\%$	$P_3/\mu A$	$\frac{P_3}{T_1}\times 100/\mu A$	$T_1/\%$	$P_3/\mu A$	$\frac{P_3}{T_1}\times 100/\mu A$	$T_1/\%$	$P_3/\mu A$	$\frac{P_3}{T_1}\times 100/\mu A$
400	0.1	0.001	1.000	49.4	0.496	1.004	0.8	0.008	1.000
410	8.5	0.018	0.212	68.1	0.146	0.214	13.0	0.028	0.215
420	45.0	0.040	0.089	70.6	0.068	0.096	53.0	0.048	0.090
430	82.5	0.047	0.057	72.3	0.044	0.061	83.8	0.053	0.061
440	86.0	0.035	0.041	74.2	0.032	0.043	87.8	0.037	0.042
450	86.7	0.021	0.024	74.5	0.019	0.026	91.2	0.026	0.028
460	86.9	0.015	0.017	75.2	0.013	0.017	93.0	0.018	0.019
470	87.0	0.011	0.013	75.2	0.009	0.012	94.1	0.016	0.017
480	87.0	0.008	0.009	75.3	0.007	0.009	94.8	0.012	0.012
490	87.3	0.006	0.007	75.3	0.005	0.007	94.8	0.008	0.008
500	87.5	0.004	0.005	75.3	0.003	0.004	94.8	0.005	0.005

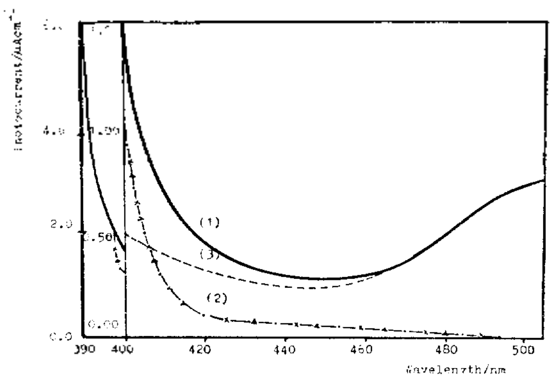

Fig. 13. Photocurrent according to transmittance of the filters for 1140(VO) TiO_{2-x} electrode in 1*M* NaOH solution. (1). ———; Without filter, (2). With filter(-×-×-×-; anthracene, -▲-▲-; $TiCl_4$ solution, -·-·-·-; TiO_2 single crystal.) (3). -----; (1)-(2).

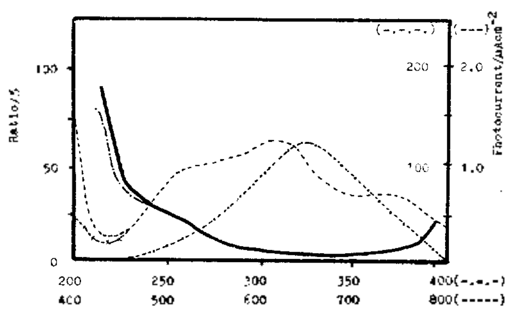

Fig. 14. Ratio of the photocurrent of the visible region (2λ) to the UV-region(λ). ---·---·; Photocurrent in the UVregion (P_0), ············; Photocurrent in the visible region (P_1), -×-×-×-; Photocurrent by second line of grating monochromator(P'_1), ———; $\frac{P_1}{P_0}\times 100$, -·-·; $\frac{P_1}{P_0}\times 100$.

in *Table* 6 and *Fig.* 10~12.

Where, T_1; the transmittance of filters in the visible-region.

The computed values of $P_2/P_0\times 100$ and $P_4/P_0 \times 100$ are summerized in *Table* 7, 8 and shown in *Fig.* 13, 14.

From the results, the peak current in vicinity of 520nm, 620nm, and 740nm within visible region responses to the second-order lines from the grating monochromator that was used, in contradiction to the proposal presented in the previous work.[9,10]

Thus, the only photoresponse of TiO_{2-x} electrode observed in the visible region are the tailing portion of 320nm peak as reported in the literature[8].

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Table 7. Ratio of the photocurrent in the UV-region (λ) and visible-region (2λ)

Wavelength (/nm)	Photocurrent ($P_0/\mu A$)	Wavelength (/nm)	Photocurrent ($P_2/\mu A$)	$P_4/\mu A$	$\frac{P_2}{P_0}\times100(\%)$	$\frac{P_4}{P_0}\times100(\%)$
200	1.25	400	1.501	0.501	120.0	40.1
205	1.32	410	0.560	0.348	42.4	26.4
210	1.40	420	0.428	0.318	30.6	22.7
215	1.75	430	0.330	0.273	18.9	15.6
220	2.00	440	0.298	0.247	14.9	12.4
225	3.10	450	0.281	0.256	9.1	8.3
230	3.90	460	0.299	0.282	7.7	7.2
235	5.70	470	0.391	0.378	6.8	6.6
240	8.20	480	0.531	0.522	6.5	6.4
245	10.90	490	0.661	0.654	6.1	6.0
250	13.60	500	0.780	0.776	5.7	5.7
255	16.80	510	0.862	0.862	5.1	5.1
260	20.40	520	0.941	0.941	4.6	4.6
265	24.60	530	0.976	0.976	4.0	4.0
270	29.50	540	1.005	1.005	3.4	3.4
275	36.00	550	1.015	1.015	2.8	2.8
280	43.60	560	1.305	1.035	2.4	2.4
285	52.50	570	1.069	1.069	2.0	2.0
290	61.80	580	1.093	1.093	1.8	1.8
295	72.20	590	1.135	1.135	1.6	1.6
300	83.0	600	1.190	1.190	1.4	1.4
305	94.0	617	1.250	1.250	1.3	1.3
310	103.1	620	1.200	1.270	1.2	1.2
315	112.5	630	1.234	1.234	1.1	1.1
320	123.2	640	1.160	1.160	1.0	1.0
325	123.5	650	1.041	1.041	0.8	0.8
330	121.5	660	0.932	0.932	0.8	0.8
335	117.0	670	0.860	0.860	0.7	0.7
340	110.5	680	0.776	0.776	0.7	0.7
345	103.2	690	0.720	0.720	0.7	0.7
350	95.5	700	0.705	0.705	0.7	0.7
355	87.0	710	0.694	0.694	0.8	0.8
360	79.5	720	0.695	0.695	0.9	0.1
365	70.5	730	0.701	0.701	1.0	1.0
370	61.5	740	0.705	0.705	1.1	1.1
375	52.0	750	0.693	0.693	1.3	1.3
380	41.5	760	0.660	0.660	1.6	1.6
385	30.5	770	0.595	0.595	2.0	2.0
390	6.8	780	0.526	0.526	7.7	7.7
395	3.4	790	0.450	0.450	13.2	13.2
400	1.5	800	0.385	0.385	25.3	25.3

P_4; Photocurrent by second order of the UV-region.

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