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Effects of loading niobium compounds on sensing factor and function of TiO_2

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Abstract

The intensity of an ESR signal assigned to oxygen species or lattice defects was increased by photo-irradiation in Nb-doped TiO_2. The excess electron was generated in the process of the formation of O^- species or lattice defects on the surface layer of the sample. On the other hand, the rise of electric current appeared on the Nb-doped TiO_2 by photo-irradiation. This behavior suggests that the generated electron by photo-irradiation is closely correlated to the rise of the current. The niobium-doped TiO_2 was found to have the performance of oxygen-sensing. The oxygen-sensing under photo-irradiation was related to the paramagnetic behavior of oxygen introduced. In addition, NO-sensing was also observed for the Nb-doped TiO_2. The function for oxygen-sensing was improved by a heat-treatment for the sample of Nb complex-doped TiO_2.

Keywords: Niobium; Sensing factor; Titanium oxide

1. Introduction

Some semiconductive metal oxides are generally used for gas sensors [1–4]. $Nb_2O_5 \cdot nH_2O$ whose surface exhibits strong acid strength is well known for behaving as acid catalyst [5,6]. Niobium oxide is also known as n-type semiconductor. Peng et al. [7] reported that binary metal oxides, such as Nb_2O_5–TiO_2, show higher sensitivities in oxygen sensing than the single oxides, TiO_2 or Nb_2O_5. This advantage of the binary oxide is due to the presence of $TiNb_2O_7$, formed by compounding Nb_2O_5 and TiO_2, in an impurity level. The present authors previously reported the oxygen-sensing factor of TiO_2 doped with metal ions [8]. Oxygen-sensing appeared under photo-irradiation on Ta_2O_5-doped TiO_2, whereas no oxygen sensitivity was observed on TiO_2 under the irradiation. In the present study, the electroconductivities with adsorption of several gaseous molecules on Nb_2O_5–TiO_2 are measured under photo-irradiation. Not only the gas-sensing factor and function of Nb-doped TiO_2, but also the effect of photo-irradiation on the character of Nb-doped TiO_2 will be reported. Furthermore, the niobium-β-diketonato complex is newly synthesized, and the effect of the control in the distance of Nb to the surface of TiO_2 on its surface properties will be also investigated.

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2. Experimental

$TiO_2(1)$ (a reference sample of Japan Catalysis Association: JRC TIO-1) of anatase-type and $TiO_2(2)$ (a reference sample of Japan Catalysis Association: JRC TIO-3) of the rutile type were used as the supports of niobium compounds. The titanium oxides were pretreated in air at 873 K for 3 h. Niobium-doped TiO_2 was prepared by impregnating the titania powder with the oxalic acid solution of 0.2 mol/l containing 5 wt.% of niobium, dried at 383 K for 24 h and calcined in air at 573 K for 3 h. Niobium complex ($Nb(dbm)_4^+-Cl^-$, Hdbm: 1,3-diphenyl-1,3-propanedione)-doped TiO_2 was prepared as follows. Niobium pentachloride and Hdbm were dissolved in dichloromethane, respectively. Hdbm solution was mixed to $NbCl_5$ solution, and the mixture was heated at 323 K. After 24 h, the complex formed was filtered off. The complex thus obtained was dissolved in acetonitrile. $TiO_2(1)$ powder was added into the acetonitrile solution and the solvent was evaporated until the complex was deposited on the surface of $TiO_2(1)$. After the rest of solvent was filtrated, the powder was washed with ether, and calcined at 573 K or 873 K in air for the measurement of conductivity. The sintered samples for the measurement of sensing function were moulded out of the disk with 0.2 g of sample, and calcined at 873 K in air. This sample was attached by a pair of Sn film electrode. A gap between the electrodes was 3 mm. The measurement of electric conductivity of the sample was performed with the electrocurrent meter by an applied voltage of 2.0 V D.C. in the dark or under photo-irradiation (with 100 V–150 W halogen lamp) either in vacuo or in the presence of oxygen or nitrogen monoxide. ESR spectra were recorded in the X-band mode with an in situ cell made of quarts at room temperature or 77 K.

3. Results and discussion

3.1. Paramagnetic behavior

ESR signals, one of $g = 1.990$ attributable to lattice defects and the other of $g = 2.006$ seemingly assignable to Fe ion or S species of impurity were observed for the sample of the powdered Nb-doped $TiO_2(1)$ (Fig. 1a), and for the neat $TiO_2(1)$ as well. In the case of $TiO_2(1)$, no change of signal intensity or shape was observed at $g = 1.990$ and at $g = 2.006$ in vacuo under the photo-irradiation. The signal intensity of $g = 1.990$ observed for Nb-doped $TiO_2(1)$ was enlarged after photo-irradiation as shown in Fig. 1b.

As depicted in Fig. 2, the signal intensity of

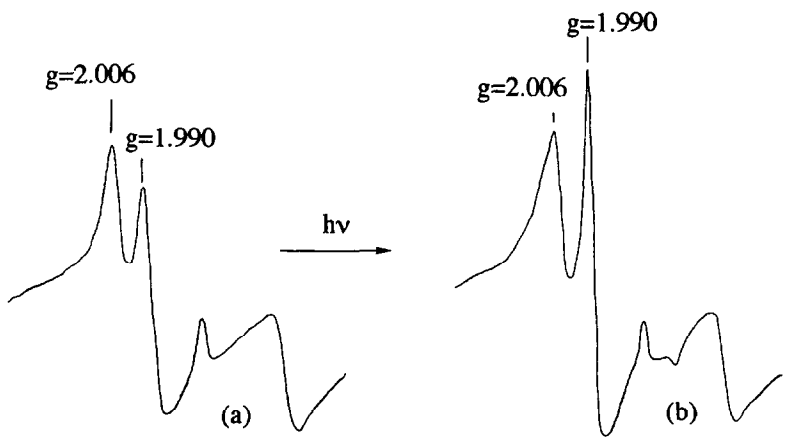

Fig. 1. ESR signal on Nb-doped $TiO_2(1)$ measured at 77 K (a) in vacuo, and (b) after photo-irradiation in vacuo.

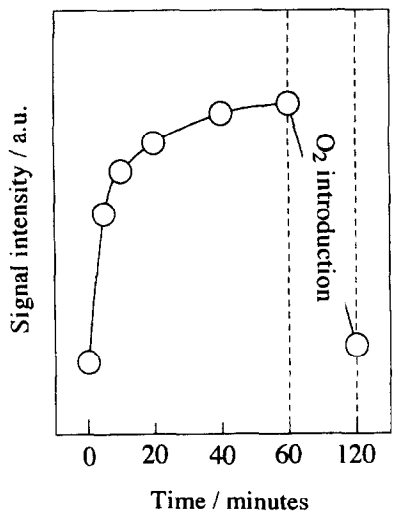

Fig. 2. Variation of ESR signal intensity of g = 1.990 on Nb-doped TiO_2(1) under photo-irradiation.

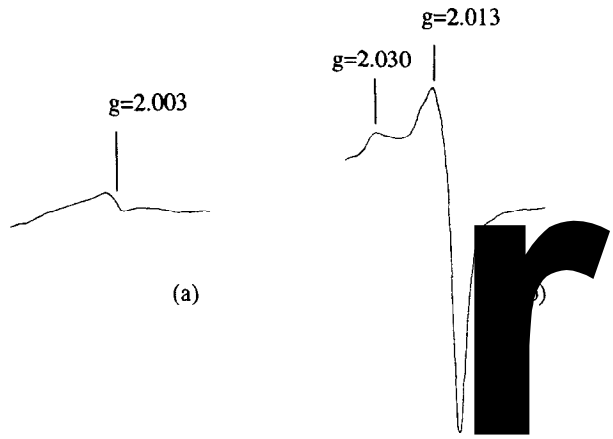

Fig. 3. ESR signal of Nb_2O_5 doped TiO_2(2) measured at 77 K (a) in vacuo, (b) after the photo-irradiation in vacuo.

$g = 1.990$ became larger with the elapse of the photoirradiation time, and decreased with oxygen introduction under photo-irradiation. Therefore, it is stressed that the increase of the signal intensity of $g = 1.990$ under the irradiation was attributed to the disappearance of oxygen from the sample through the desorption or dissociation of oxygen by photo-irradiation in vacuo. The decrease of the signal intensity with oxygen introduction under photo-irradiation was caused by the readsorption of oxygen or the recombination of the dissociated oxygen atoms on the surface of sample. The signal intensity of $g = 1.990$ also decreased with NO introduction under photo-irradiation.

In Nb-doped TiO_2(2), ESR signal of $g = 2.003$ appeared in vacuo. This signal seemed to be assigned to oxygen species. As shown in Fig. 3, the shape of the signal was changed by photo-irradiation. Che and Tench [9] and Morikawa et al. [10] have reported the formation of O_3^-. The shape of this signal is similar to that of the O_3^-, so O_3^- was formed by photo-irradiation on Nb-doped TiO_2(2). Therefore, one of the double bond of Nb=O must be broken on TiO_2(2) by photo-irradiation and changed into $Nb–O^-$ species. On the photo-irradiation, O_3^- species was formed by which the photo-desorbed oxygen was photo-adsorbed on $Nb–O^-$ species.

The unsymmetrical signals of $g = 2.023$, $g = 2.010$, and $g = 2.007$ were observed in Nb-doped TiO_2(2) when oxygen was introduced under the photo-irradiation or dark, as shown in Fig. 4. According to the g values and the shape of the signals, these are due to the adsorbed O_2^- species. Thus, the surface O^- species generated by the photo-irradiation may play a site of the

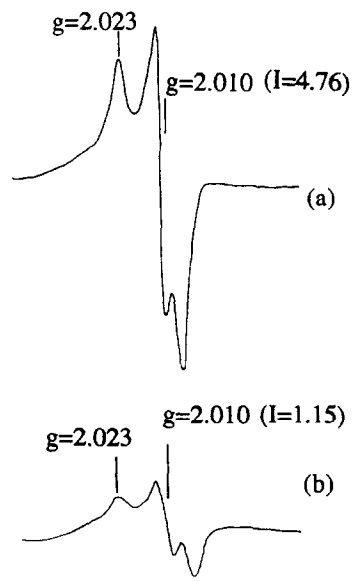

Fig. 4. ESR signal of Nb-doped TiO_2(2) adsorbed O_2 (a) under photo-irradiation and (b) in the dark.

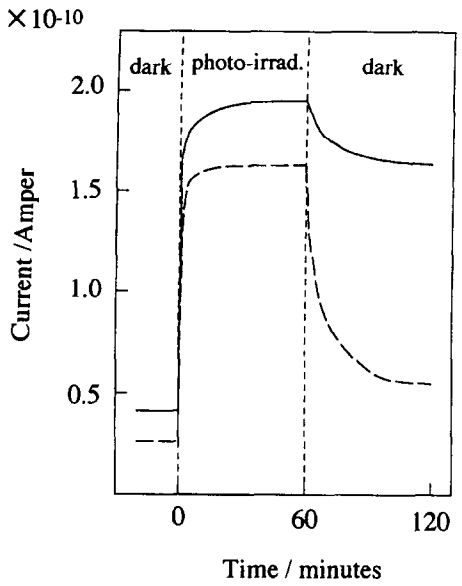

Fig. 5. Rise and decay curve of electroconductivity on $TiO_2(1)$ (broken line) and Nb-doped $TiO_2(1)$ (solid line) in vacuo.

O_2 adsorption or of the reaction of O_2 to form the O_2^- species. The intensity of signal at $g = 2.003$ was also decreased with the additional introduction of NO.

3.2. The characteristics of photo-electroconductivity

In the measurement of the electroconductivity under dark conditions for $TiO_2(1)$ and for Nb-doped $TiO_2(1)$ the values of current, 2.6×10^{-11} and 4.2×10^{-11} A were observed, respectively. Since the dark current for Nb-doped $TiO_2(1)$ was higher than that for $TiO_2(1)$, the conduction electrons must be generated through the substitution of Ti^{4+} substituted by Nb^{5+} and/or the formation of the complex such as $TiO_2/Nb_2O_5/TiO_2$. These samples showed photo-conductivity.

The variations in the current for $TiO_2(1)$ and Nb-doped $TiO_2(1)$ are exhibited in Fig. 5. The photo-current attained an equilibrium value within approximately 10 min in the case of $TiO_2(1)$. Nb-doped $TiO_2(1)$ took a long time in comparison with $TiO_2(1)$ to attain the equilibrium in the photo-current. This implies that on the surface of Nb-doped TiO_2 a certain chemical reaction occurs such as the photo-elimination of oxygen.

As the paramagnetic behavior mentioned above, $Nb-O^-$ species was formed by photo-irradiation according to Eq. (1),

$$TiO_2\text{---}Nb^{5+} = O^{2-} + h\nu \rightarrow TiO_2\text{---}Nb^{4+} - O^- \quad (1)$$

Then, the photo-elimination of oxygen occurred as

$$TiO_2\text{---}Nb^{4+} - O^- + h\nu \rightarrow (TiO_2 + 2e)\text{---}Nb^{5+} + \tfrac{1}{2}O_2 \quad (2)$$

The photo-decomposition of Nb=O bond as expressed by Eqs. (1) and (2) in Nb-doped TiO_2 results in the generation of the photo-electron, caused to the rise in the current. Through the examination of the decay curve for the current obtained for the photo-irradiation interception after the photo-irradiation for 1 h in vacuo, the value of the current for $TiO_2(1)$ gradually decreased and returned nearby to the original value of the dark current. On the other hand, the photo-current of Nb-doped $TiO_2(1)$ slightly fell after the cease of the photo-irradiation and did not revert to the original value. These results suggests that the decrease of the current for $TiO_2(1)$ is due to the recombination between electron and hole which are generated by the photo-irradiation, while that for Nb-doped $TiO_2(1)$ may be resulted from its photo-reduction including a certain irreversible process.

3.3. The function of oxygen sensing

The variation of the photoconductive current induced by the oxygen introduction (after photo-irradiation for 1 h) was shown in Fig. 6. In the presence of oxygen, the current observed for $TiO_2(1)$ rapidly diminished, when the photo-irradiation was intercepted, but did not vary during the photo-irradiation. In the case of the photo-interception, the diminution of the

current is caused by the combination of a conduction electron, e^-, and an introduced oxygen molecule as

$$O_2 + e^- \rightarrow O_2^-(ad) \quad (3)$$

followed by the combination of O_2^- with a hole, h^+, as

$$O_2^-(ad) + h^+ \rightarrow O_2 \quad (4)$$

Under the photo-irradiation, no change in the current was observed for the oxygen introduction, suggesting that the processes expressed by Eqs. (3) and (4), equivalent to the recombination of an electron and a hole, were equilibrated with these photo-formation under the photo-irradiation in the presence of oxygen.

Evidently, the value of the current was even decreased under the photo-irradiation by the oxygen introduction in the case of Nb-doped $TiO_2(1)$ as shown in Fig. 7, not observed for TiO_2. In the presence of oxygen, the reverse reaction of Eq. (2) without the photo-irradiation can occur easily, resulting in the current decrease under the photo-irradiation. When Nb is doped on TiO_2, the latter sample shows the function of sensing to oxygen, caused by the photo-adsorption and elimination of oxygen on its surface. The oxygen introduction to the sample induces the diminution of the electric conduction current, usually accelerated by photo-irradiation. The degree of the current diminution, denoted by D, is evaluated by the equation,

$$D = (I_p - I_i)/(I_p - I_d)$$

where I_p, I_d, and I_i are the current at the photo-irradiation time of 1 h, dark current (original current) and the current at the time of i min after the introduction of gas, respectively. The current for Nb-doped $TiO_2(1)$ with oxygen introduction was equilibrated during about 10 min under photo-irradiation. The degree of the current diminution, D, was 0.5. The generation of conduction electron is not only concerned with the generation of electron and hole but also the photo-elimination of surface oxygen by photo-irradiation. The decrease of the current is responsible for recombination of introduced oxygen to the site which has released oxygen on the surface of the sample. The diminution, D, was 0.01 after 1 min of photo-interception in the absence of oxygen, while 0.14 in the presence of oxygen, and 0.25 under photo-irradiation in the presence of oxygen. It is implied that

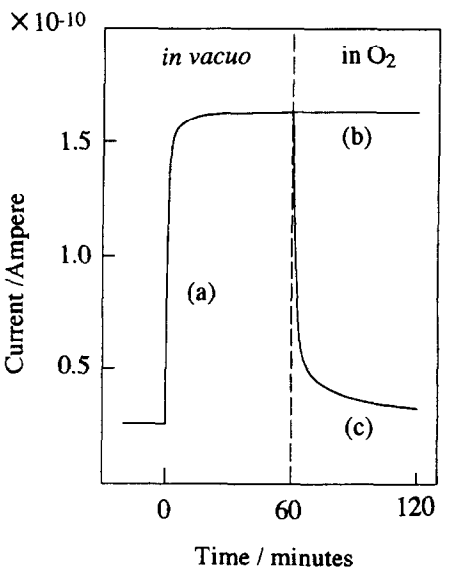

Fig. 6. Variation of electroconductivity on $TiO_2(1)$ (a), (b) under photo-irradiation and (c) in the dark.

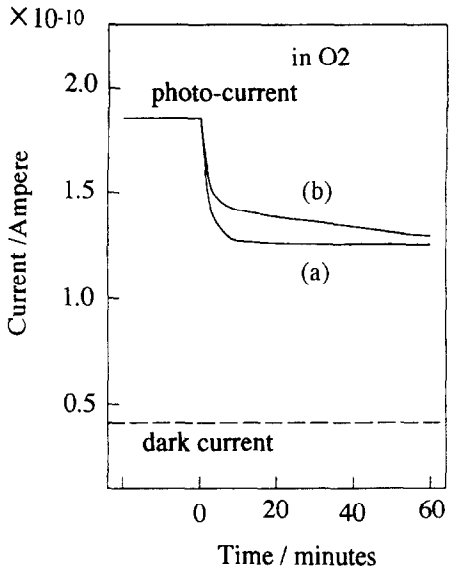

Fig. 7. Decrease of current on Nb–$TiO_2(1)$ (a) under photo-irradiation and (b) in the dark.

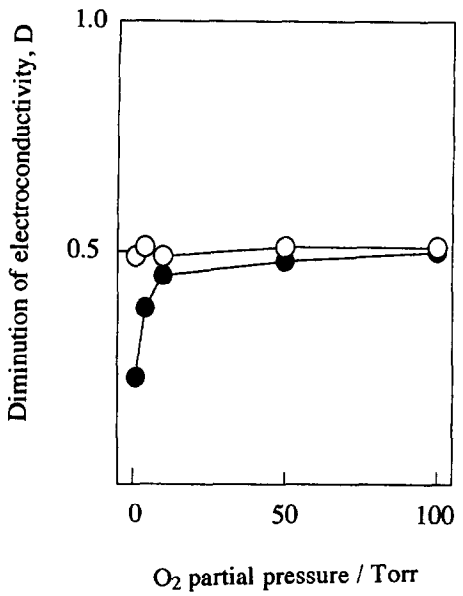

Fig. 8. Dependence of diminution in the electroconductivity of Nb-doped TiO_2, D, upon O_2 partial pressure. ○: under photo-irradiation, ●: in the dark. The values of D were determined at the time of one h after the introduction of oxygen.

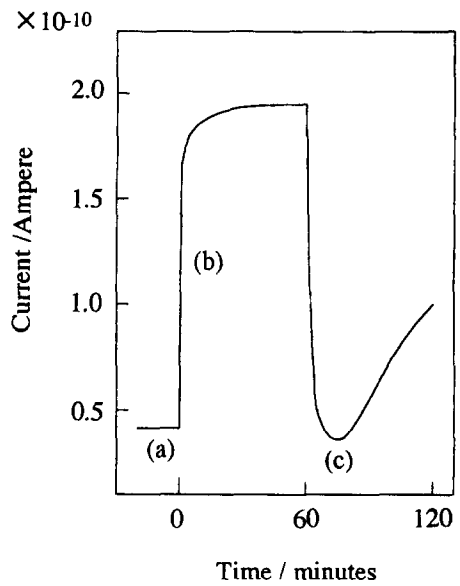

Fig. 9. Variation of electroconductivity on Nb-doped $TiO_2(1)$ (a) in the dark in vacuo, (b) under photo-irradiation in vacuo and (c) in the presence of NO under photo-irradiation.

the response time for the current to the oxygen introduction is the most rapid in the presence of oxygen under photo-irradiation.

The diminution, D, was dependent on the oxygen pressure introduced as shown in Fig. 8. Under photo-interception the value of D was greatly varied where the oxygen pressure was less than 10 Torr, and reached a constant value over 10 Torr. On the other hand, it was not dependent on the oxygen pressure under photo-irradiation.

The feature of the current change for Nb-doped $TiO_2(2)$ was similar to that for Nb-doped $TiO_2(1)$, showing a D value of 0.18 in the presence of oxygen under photo-irradiation. The smaller value than that observed for Nb-doped $TiO_2(1)$, may be attributed to the low rate of photo-elimination of oxygen because of the small surface area of $TiO_2(2)$.

3.4. The function of NO sensing

When nitric oxide was introduced onto Nb-doped $TiO_2(1)$ under photo-irradiation, the value of the current was greatly reduced as exhibited in Fig. 9. The neat $TiO_2(1)$ also showed a diminished electro-conductivity. The degree of

Table 1
Effects of the heat-treatment for the degree of the photosensitivity and of the diminution for Nb-doped $TiO_2(1)$

Temperature of heat-treatment (K)	Degree of photosensitivity	Degree of diminution after O_2 introduction (D)		
		1 min	10 min	60 min
Nb-doped $TiO_2(1)$ [a]				
573	4.2	0.25	0.38	0.50
Nb complex-doped $TiO_2(1)$ [b]				
573	6182	0.84	0.98	0.99
873	2436	0.65	0.95	0.98

[a] Niobium oxalate (starting material).
[b] Niobium $(dbm)_4 + Cl^-$ (starting material).

the diminution of Nb-doped TiO_2(1) was larger than that of TiO_2(1) in the preence of NO. The current once diminished nearly to the original current gradually recovered in the case of Nb-doped TiO_2(1), indicating that the current decreased by the NO adsorption on the sample surface was recovered through the reduction of niobium oxide on the surface of TiO_2 by NO. Similar behaviour was observed in the case of Nb-doped TiO_2(2). Thus, niobium-doped TiO_2 has the function for NO-sensing.

3.5. Sensing function of Nb complex-doped TiO_2

The photosensitivity for the heat-treated Nb complex-doped TiO_2(1) was advantageous appreciably in comparison with Nb-doped TiO_2. The degree of the photosensitivity was evaluated by the equation,

$$P_S = (I_p - I_d)/I_d$$

The advantage of the photosensitivity was different by means of the heat treatment as summarized in Table 1. The quantity of niobium contained in the niobium complex-doped TiO_2(1) heat-treated at 873 K was 6 wt.%, and that at 573 K was 14 wt.%. The difference in the Nb quantities was caused by the sublimation property of the complex. The photosensitivity is larger in the more quantity of Nb in the sample. When oxygen was introduced on the samples under photo-irradiation, the current reduced greatly and came nearly to the dark current. When the niobium complex-doped TiO_2(1) was heat-treated, the photosensitivity was greatly improved and the function of oxygen-sensing was also enlarged. For NO introduction, the current for the heat-treated niobium complex-doped sample was diminished nearly to the dark current, and no recovery of the current was observed in contrast to the case of Nb-doped TiO_2(1). For the introduction of oxygen under dark, the degree of the diminution of the electroconductive current was about 1 regardless of the value of oxygen pressure. Under photo-irradiation, the degree of the diminution by the oxygen introduction was roughly linear to the oxygen pressure of about less than 30 Torr.

4. Conclusion

On Nb-doped TiO_2, the existence of O^-, O_2^-, O_3^-, and lattice defects were observed by the measurement of ESR. The oxygen molecule and the photo-electron was generated by the photo-reduction of TiO_2–$Nb^{4+}O^-$ species. This photo-electron caused to a rise in the conductive current of the sample. The function of oxygen-sensing appeared newly under photo-irradiation when niobium was doped on TiO_2. Nb-doped TiO_2 showed the function of NO sensing, while the slight decrease for the current was detected with NO introduction under photo-irradiation for neat TiO_2. The heat-treated Nb complex-doped TiO_2 was advantageous in the photosensitivity and the function of oxygen-sensing.

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