

Photoelectrochemical Behavior of Nb-Doped TiO₂ Electrodes

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The photoelectrochemical behavior of **degenerate** Nb-doped TiO₂ (Ti_{1-x}Nb_xO₂; $x = 0, 0.01, 0.03, 0.06, 0.1$) electrodes prepared by pulsed laser deposition on LaAlO₃ (LAO) and SrTiO₃ (STO) was examined, revealing that an increase in Nb concentration causes a significant decay of titania photoactivity. One reason for such behavior may be a Burstein–Moss effect, which leads to a blue shift of the spectral limit of photoactivity. Another reason typical for metal-doped photocatalysts is the increase of the efficiency of charge carrier recombination.

Introduction

Since the discovery of the photoelectrochemical splitting of water on a titania electrode by Honda and Fujishima some two decades ago,¹ major research efforts have focused on the problem of increasing the efficiency of photoelectrochemical processes. Metal and nonmetal ion doping of TiO₂ have been studied extensively in photoelectrochemistry and in photocatalysis to achieve higher activities and spectral sensitivities of titania.^{2–6} Despite the relatively long history of studies of metal-doping modification of titania, only a few reports might be considered as having had some success thus far. The major reason for this lack of success is probably the higher efficiency of electron–hole recombination in metal-doped titania as a result of the formation of new types of defects.^{2–4,7}

New methods of synthesis and major properties of new heavily Nb-doped TiO₂ materials have been reported recently.⁸ It was demonstrated that extensive doping of titania with Nb turned an otherwise n-type semiconductor into a degenerate semiconductor with high metallic-like conductivity. This was explained in terms of formation of an impurity band overlapping with the conduction band of titania.

The present article reports our recent results of an experimental photoelectrochemical study of the same set of heavily Nb-doped Ti_{1-x}Nb_xO₂ films (where $x = 0.01, 0.03, 0.06$, and 0.1 ; film thickness, $1.2\ \mu\text{m}$).

Experimental Section

The Nb-doped titania samples were prepared by pulsed laser deposition on LaAlO₃ (LAO) and SrTiO₃ (STO) by a procedure described elsewhere.⁸ All Nb-doped samples belong to the class of degenerate semiconductors with a metallic type of conductivity and concentration of free electrons in the conduction band 10^{21} – $10^{22}\ \text{cm}^{-3}$, directly proportional to the content of Nb ions in samples.⁸ Sample plates ($5 \times 5\ \text{mm}^2$) were used to make electrodes with a working area of about $15\ \text{mm}^2$. Measurements were carried out with a standard three-electrode system that included an SCE reference electrode and a Pt counter electrode connected to a Hokuto Denko HZ-5000 potentiostat. The electrolyte solution ($0.1\ \text{M KCl}$) was prepared with reagent grade chemical and Milli-Q water; it was mechanically stirred and

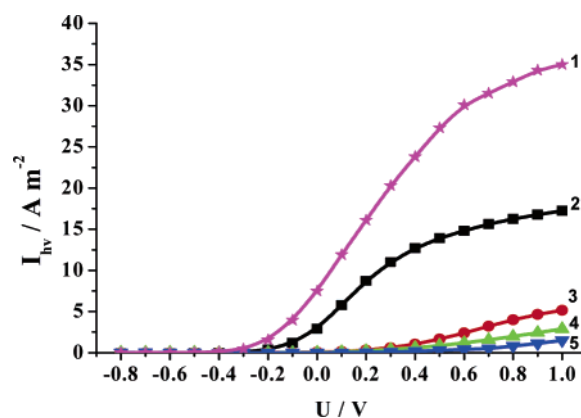


Figure 1. Experimental dependencies of stationary photocurrent on applied voltage for Ti_{1-x}Nb_xO₂ grown on LAO electrodes: (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.03$; (4) $x = 0.06$; and (5) $x = 0.1$.

purged with nitrogen prior to and during the experiments. Irradiation of the sample electrode was carried out through the cell quartz-window with either a 150-W Xe lamp (Hayashi LA-251Xe) or in the case of spectral measurements with a 300-W Xe lamp (Oriol MLH-300) combined with a monochromator (Oriol Corner Stone). In the latter case, the spectral half-widths of the band path of the actinic light were in the range of ca. 6–8 nm. Light intensity was measured with a Nova power meter.

Results and Discussion

Figure 1 illustrates the stationary photocurrent–voltage dependencies for the set of samples examined. As evident from the experimental curves, Nb doping causes a drastic decay of the photocurrent despite the increase in the conductivity of the samples. Miyagi and co-workers⁷ showed that titania doped with Nb leads to the formation of new defects and deep electron traps, which they assumed could serve as efficient recombination centers that caused complete loss of photocatalytic activity of the modified titania samples. However, the recombination rate is expected to be faster even if the concentration of recombination centers were to remain the same because of the high concentration of electrons in the conduction band, which scales linearly with the Nb concentration. In fact, at such high values of electron concentration, band-to-band recombination with

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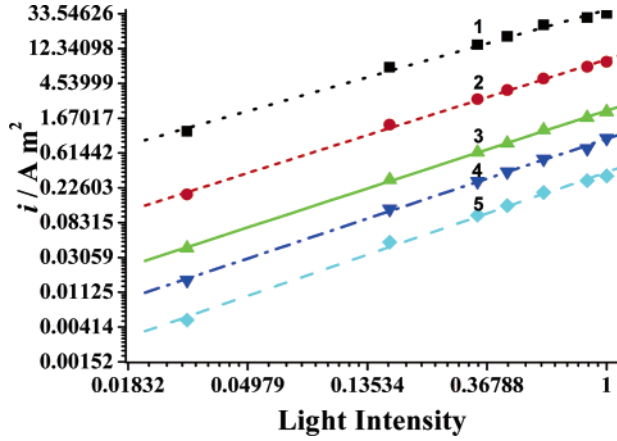


Figure 2. Dependencies of stationary photocurrent on light intensity for $\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ grown on LAO electrodes: (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.03$; (4) $x = 0.06$; and (5) $x = 0.1$ at 0.5 V applied voltage.

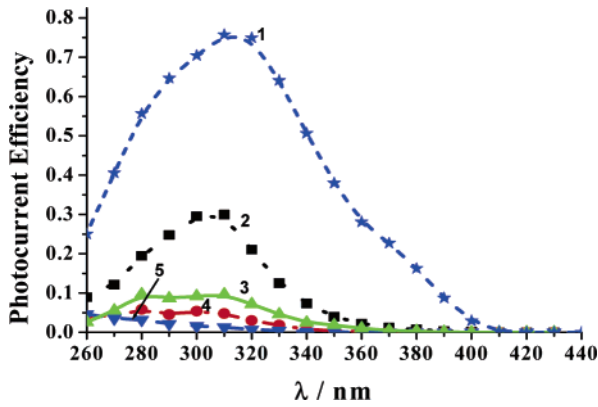


Figure 3. Spectral dependencies of photocurrent efficiency for $\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ grown on LAO electrodes: (1) $x = 0$; (2) $x = 0.01$; (3) $x = 0.03$; (4) $x = 0.06$; and (5) $x = 0.1$ at an applied voltage of 0.5 V.

photoholes should be quite effective compared to recombination through recombination centers. Moreover, even in the case of bimolecular electron–hole recombination, the excess of electrons should lead to a linear dependence of the photocurrent on light intensity as observed experimentally for Nb-doped titania electrodes (Figure 2) since the recombination efficiency is fully dictated by the concentration of photoholes. Obviously, this increase of electron concentration is also a factor in determining the shift of photocurrent onset toward a positive potential. However, other changes in physical properties may lead to the decrease of photocurrent caused by Nb doping. One of these is the eventual loss of carrier mobility, as demonstrated by Furubayashi and co-workers,⁸ arising from charge carrier scattering on the Nb dopant species. Another possible reason for the decay of electrode photoefficiency is the blue shift of the spectral limit of the photoresponse caused by a Burstein–Moss^{9,10} effect. The latter is a shift of the spectral limit of light absorption to higher energies because of electron-filled lower energy states in the conduction band (owing to the degeneracy of the semiconductor), which preclude additional electronic transitions to the bottom of conduction band. Indeed, such a blue shift is observed in the spectral dependencies of the photocurrent measured for the tested samples of Nb-doped titania electrodes. Figure 3 depicts the experimentally observed spectral dependencies of photoefficiency, η , determined according to the equation

$$\eta = \frac{ihc}{\lambda P e} \quad (1)$$

TABLE 1: Optical Band Gaps and Spectral Limits of the Photocurrent Determined for $\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ Grown on LAO Electrodes^a

	Nb content x in $\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$				
	0	0.01	0.03	0.06	0.1
$h\nu_{\text{onset}}$, eV	2.75	3.0	3.10	3.21	3.21
$E(\eta)_g$, eV	2.98	3.29	3.33	3.38	3.43
$E(\alpha)_g$, eV	3.21	3.34	3.38	3.43	3.46

^a $h\nu_{\text{onset}}$ is the spectral limit of photocurrent, $E(\eta)_g$ and $E(\alpha)_g$ are the optical band gaps determined from the spectral dependencies of photocurrent efficiency and absorption spectra, respectively.

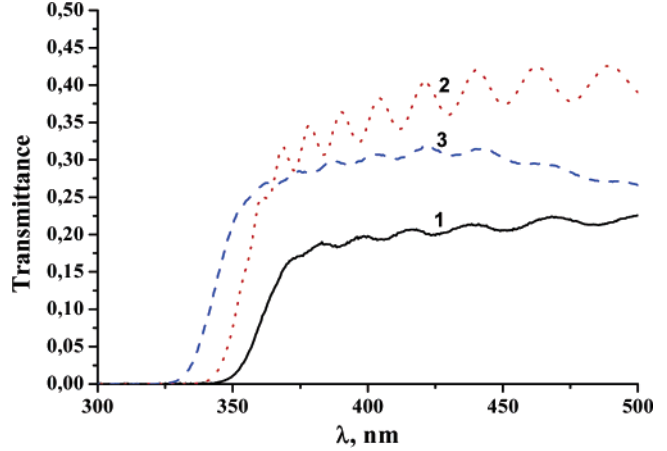


Figure 4. Transmittance spectra of $\text{Ti}_{1-x}\text{Nb}_x\text{O}_2$ grown on LAO samples: (1) $x = 0$; (2) $x = 0.03$; and (3) $x = 0.1$.

where i is the photocurrent density, h is Planck's constant, c is the velocity of light, λ is the wavelength of the incident light, and P is the light intensity. The optical band gaps $E(\eta)_g$ were determined as per eq 2, which applies to typical transitions in indirect semiconductors and is valid when the light penetration depth is longer than the diffusion length of the photocurrent and the Debye length (note that A scales inversely with photon energy and depends on both the diffusion length of the photocurrent and the Debye length).¹¹

$$\eta = A(h\nu - E_g)^2 \quad (2)$$

The results are summarized in the Table 1, together with the spectral limits $\{h\nu_{\text{onset}}\}$ of the photocurrent.

Clearly, the optical band gap increases with increasing Nb concentration. In Figure 4 we present the transmittance spectra of the samples which also demonstrate the blue shift of fundamental absorption threshold. The values of optical band gaps determined from absorption spectra of the samples $\{E(\alpha)_g\}$ by applying eq 3, which is valid for the indirect optical transitions, are reported in Table 1 and confirm the existence of the blue shift of the optical band gap in degenerate semiconductor with increase of electron concentration in the conduction band due to Nb doping.

$$\alpha = A(h\nu - E_g)^2 \quad (3)$$

However, one should note that application of eqs 2 and 3 to determine the optical band gap in degenerate semiconductors is quite arbitrary, since both equations are applicable only for band-to-band transitions from the energy states at the top of the valence band to the bottom of the conduction band provided that the hyperbolic energy distribution in momentum space is valid. We cannot claim a priori that this condition is satisfied

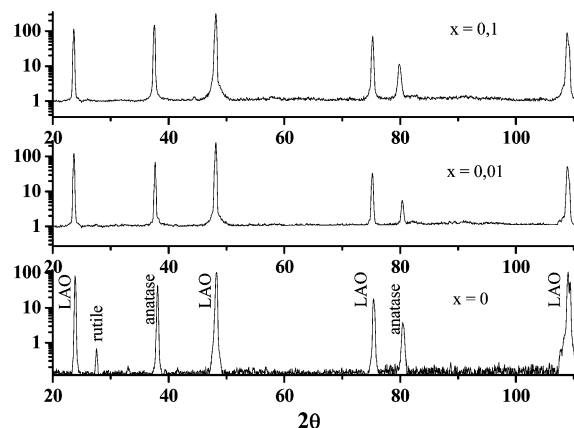


Figure 5. XRD data for Ti_{1-x}Nb_xO₂ samples grown on LAO ($x = 0, 0.01, 0.1$).

for the higher energy unoccupied states in the conduction band of Nb-doped TiO₂ samples. More, we cannot also assume that Nb doping does not change the energy distribution at the bottom of the conduction band. Therefore, data reported in Table 1 can be taken only as the approximate estimation of the optical band gaps of Nb-doped samples. However, they clearly demonstrate the tendency for the increase of the optical band gap with increase of Nb concentration in TiO₂.

The same blue shift tendency was observed for the spectral limit of the photocurrent shifted toward higher energies (Table 1). Note that for all the samples examined, the spectral limit of the photocurrent is red-shifted compared to the optical band gap energy. For the nominally pure (undoped) sample, this can be explained by photoexcitation of either defect or surface states, whereas for the Nb-doped samples the spectral limits of the photocurrent are within the energy corresponding to interband transitions. Free electron trapping by preexisting defects probably turns such defects into photoinactive states. Note also that at the higher doping level, the spectral limit of the onset of photocurrent corresponds to the band gap of the modified anatase titania, whereas for the undoped sample the optical band gap corresponds to the band gap energy for rutile titania. This is in agreement with the XRD data, which showed that the undoped sample consists of a mixture of anatase and rutile phases (see Figure 5). Evidently, Nb doping stabilizes only the anatase form. Accordingly, the spectral limit of the photocurrent in the latter case is dictated by band-to-band transition since thermoexcitation of the samples can smear the edge of the filled states in the conduction band and thus allows the existence of interband transitions with energies smaller than the apparent optical band gap.

That the Burstein–Moss effect results in a blue shift of the spectral limit of the photocurrent is a significant factor that leads to the decrease of the integrated photocurrent with increasing Nb concentration as evidenced in Figure 1.

So far, we have observed no positive effect(s) of Nb doping on the photoelectrochemical response of the modified electrodes caused by the higher conductivity of the electrodes. However, results obtained with Nb-doped titania films grown on the STO support show that some positive effect(s) can be achieved.

Figure 6 depicts the spectral dependencies for Ti_{0.97}Nb_{0.03}O₂ (where $x = 0.03$) deposited on LAO (curve 1) and on STO (curve 2) supports. An obvious difference in the spectral behavior arises from the fact that photons with energies near 3.2 eV are mainly absorbed by the STO support, since such absorption by Nb-doped titania is forbidden so that the photo-

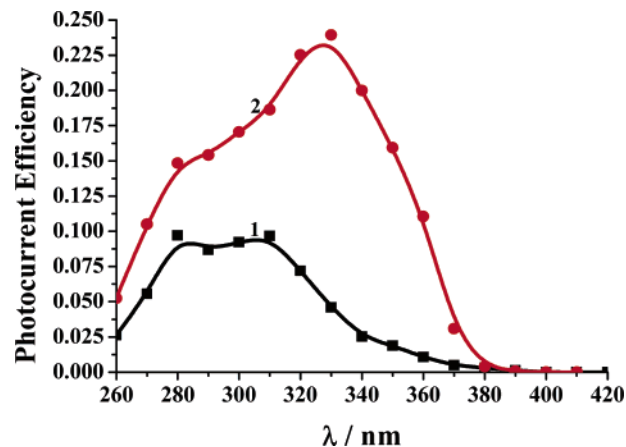


Figure 6. Spectral dependencies of photocurrent efficiency for Ti_{1-x}Nb_xO₂ electrodes ($x = 0.03$) grown on LAO (1) and on STO (2) at 0.5 V applied voltage.

carriers from STO flow through the STO–titania junction to the highly conductive titania and result in higher photocurrents compared to photocurrents originating from Nb-doped titania deposited on LAO. Thus, we deduce that Nb-doped titania serves as a good electron-transfer mediator when no photoholes are generated in the titania itself. In this case, the blue shift in absorption caused by the Burstein–Moss effect in Nb-doped titania plays a positive role preventing the photogeneration of holes within certain spectral regions.

Conclusion

In summary, we conclude that heavy Nb doping causes a negative tendency in the photoelectrochemical activity of titania electrodes in photochemical processes. There exist three major reasons for such an effect: (1) formation of new recombination centers induced by Nb doping that increases the efficiency of recombination decay of photoholes, (2) high concentration of electrons donated by Nb in the conduction band that increases the efficiency of band-to-band recombination with photoholes, and (3) transformation of an otherwise n-type semiconductor into a degenerate semiconductor caused by Nb doping that decreases the fraction of light absorbed by photoelectrode due to the Burstein–Moss effect, which leads to a blue shift of the optical band gap.

However, Nb doping plays a definite positive role if the modified titania were used as an electron-transfer mediator. Accordingly, one can expect that Nb-doped titania is an attractive material to act as a mediator in dye-sensitized and solid-state-type solar cells provided that no photoholes are generated in the titania.

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