

## TiO<sub>2</sub> 光催化薄膜的 XPS 研究 \*

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**摘 要** 利用 TiO<sub>2</sub> 溶胶通过浸涂技术在钠钙玻璃表面制备了 TiO<sub>2</sub> 光催化薄膜, 根据 X 射线光电子能谱 (XPS) 对薄膜进行了表征. 结果表明, 薄膜中除含有 +4 价 Ti 的氧化物外, 还有一定量的 +3 和 +2 价 Ti 的氧化物. 结合有机基团燃烧的还原作用、玻璃中钠与钙离子的扩散和 Ar 离子刻蚀, 对这种现象作了讨论. O1s 的高分辨谱比文献报道的更复杂. 元素在薄膜内层的分布更均匀, 从表面到内层, O 和 Ti 元素的含量明显增加, 而 C、Na 和 Ca 元素的浓度下降.

**关键词** TiO<sub>2</sub> 薄膜 溶胶-凝胶法 XPS 价态

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## XPS STUDY ON TiO<sub>2</sub> PHOTOCATALYTIC THIN FILM PREPARED BY THE SOL-GEL METHOD

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**ABSTRACT** TiO<sub>2</sub> photocatalytic thin films on a soda-lime glass substrate were prepared by a dip-coating technique using TiO<sub>2</sub> sol solution and characterized by X-ray photoelectron spectroscopy (XPS). The results showed that besides oxides of Ti(IV) there was a certain amount of oxides of Ti(III) and Ti(II). The phenomenon was discussed in relation to the reduction of residual carbons from organic radicals, the conditions of argon-ion sputtering and the diffusion of sodium and calcium ions from the glass substrates. The spectra of O1s were more complicated than those of O1s reported previously in literature, and elements were comparatively uniformly distributed in depth, while there were obvious increases in titanium and oxygen contents and decreases in the concentrations of carbon, sodium and calcium from the surface to the depth.

**KEY WORDS** TiO<sub>2</sub> thin films, sol-gel method, XPS, valency state

In recent years, many works have been focused on the application of TiO<sub>2</sub> thin film photocatalyst in purification and treatment of air and water<sup>[1,2]</sup>. Because of easy recovery and no pollution

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after the reaction, there were more and more research papers on  $\text{TiO}_2$  thin film photocatalyst. A few papers<sup>[2~4]</sup> described  $\text{TiO}_2$  thin films showing activity as high as  $\text{TiO}_2$  fine powders. Photocatalytic chemical reactions occurring on the surface of  $\text{TiO}_2$  thin films were predominantly determined by fundamental surface properties of  $\text{TiO}_2$  thin films. It is necessary for scientists handling photocatalyst to clarify the important factors which affected the activity. A prospective method with good results shown in practice in this type of investigation is X-ray photoelectron spectroscopy (XPS)<sup>[5]</sup>. There were some data in the literatures on XPS investigation of  $\text{TiO}_2$  thin films. For example, Pouilleau et al.<sup>[6]</sup> investigated the electrochemical behaviors of the magnetic phase titanium oxide with the general formula  $\text{Ti}_x\text{O}_{2x-1}$  and surface analysis of these ceramic electrodes by XPS. Trapalis et al.<sup>[7]</sup> studied the chemical compositions and valency states of elements in titanium-based coatings modified by  $\text{SnO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{SiO}_2$  through XPS. However, there were few data in the literature on XPS investigations of  $\text{TiO}_2$  thin film photocatalyst.

There were also different viewpoints on the valency state of titanium in the  $\text{TiO}_2$  thin films prepared by sol-gel method<sup>[7,8]</sup>. In the present work, the sol-gel method was employed to prepare  $\text{TiO}_2$  thin films, and the chemical compositions and valency states of elements on the surface and in depth of the films were quantitatively analyzed by XPS. The behavior of Ti and O elements in the films was discussed on the basis of binding energy.

## 1. Experimental Details

### 1.1 Preparation of $\text{TiO}_2$ thin films

Precursor solutions for  $\text{TiO}_2$  thin films were prepared by the following method<sup>[3,4]</sup>. Tetrabutylorthotitanate (17.02mL) and diethanolamine (4.8mL) were dissolved in ethanol (67.28mL). After stirring vigorously for 2 h at room temperature, a mixed solution of water (0.9mL) and ethanol (10mL) was added dropwise to the above solution with a burette under stirring. The resultant alkoxide solution was kept standing at room temperature for hydrolysis reaction for 2 h, resulting in the  $\text{TiO}_2$  sol. The composition ratio of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2\text{O}$  and  $\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$  in the starting alkoxide solution was 1:26.5:1:1 (in molar ratio). Soda-lime glass plates (75mm  $\times$  25mm  $\times$  1.5mm) were used as the substrates for thin films. Gel films were formed on the substrates from the coating solution by dipping-withdrawing in an ambient atmosphere and heat-treated at 500  $^\circ\text{C}$  for 1 h in air using an electric oven. The withdrawing speed was 1 mm $\cdot$ s<sup>-1</sup>. The thickness of the  $\text{TiO}_2$  films was adjusted by repeating the cycles from withdrawing to heat-treatment. The thickness of a mono- $\text{TiO}_2$  thin film was estimated to be about 0.12  $\mu\text{m}$  by SEM observation of the cross-sections.

### 1.2 XPS measurement of $\text{TiO}_2$ thin film

The mono- $\text{TiO}_2$  thin film was analyzed by XPS, using a VG Scientific ESCALAB Mark II spectrometer equipped with two ultrahigh-vacuum (UHV) chambers, the pressure in the chambers during the experiments was about  $10^{-7}$ Pa. A  $\text{MgK}\alpha$  X-ray source was used. The analyzer was operated at 20eV pass energy for high resolution spectra and 50eV for survey spectra. The X-ray photoelectron spectra were referenced to the C1s peak ( $E_b=284.80\text{eV}$ ) resulting from the

adventitious hydrocarbon (i.e. from the XPS instrument itself) present on the sample surface. The depth profile experiments were done by sputter-etching the thin film for 300 s and 600 s using 5 keV argon-ions at a beam current of 20~40mA.

## 2. Results and Discussion

### 2.1 Survey spectra

The survey spectrum (Fig.1) showed that there were Ti, O, C, Ca and Na elements on the surface of the film. The Ti and O elements resulted from the precursor solution. The C element probably came from the organic radicals of precursor solution for sol-gel method, which were not completely burnt out during heat-treatment and the adventitious hydrocarbon. The Na and Ca elements resulted from the atomic diffusion from the glass substrate.

### 2.2 High resolution XPS spectra

**2.2.1 The Ti2p region** The high resolution XPS spectra of the Ti2p taken at the sample surface and at depth after sputtering for 600 s were shown in Fig.2. The Ti2p region can

be decomposed into several contributions corresponding to the different oxidation states of titanium. Each contribution consisted of a doublet between the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> peaks. For each doublet, the ratio of the area of the two peaks  $A(\text{Ti}2p_{1/2}) / A(\text{Ti}2p_{3/2})$  was equal to 0.5 and the binding energy difference,  $\Delta E_b = E_b(\text{Ti}2p_{1/2}) - E_b(\text{Ti}2p_{3/2})$  was always 5.7eV, as previously reported in the literature<sup>[9]</sup>.

The high resolution XPS spectrum corresponding to the surface was characterized by a main doublet composed of two symmetric peaks situated at  $E_b(\text{Ti}2p_{3/2}) = 458.30\text{eV}$  and  $E_b(\text{Ti}2p_{1/2}) = 464.05\text{eV}$ , in agreement with the literature<sup>[7,9]</sup>. This main doublet was assigned to Ti(IV) (titanium in the IV oxidation state). As shown in Fig.2(b), after sputtering for 600 s, it was found that the spectrum at depth also contained this doublet as major feature. In addition, it was also necessary to take into account two minor contributions from Ti(II) and Ti(III). They included: (a) Ti(III) from Ti<sub>2</sub>O<sub>3</sub> species, the symmetric peaks of the corresponding doublet were situated at  $E_b(\text{Ti}2p_{3/2}) = 457.55\text{eV}$  and  $E_b(\text{Ti}2p_{1/2}) = 463.30\text{eV}$ , as reported in the literature<sup>[6]</sup>. (b) Ti(II) from TiO species. The two symmetric peaks of the doublet have the following binding energies:  $E_b(\text{Ti}2p_{3/2}) = 456.35\text{eV}$  and  $E_b(\text{Ti}2p_{1/2}) = 462.05\text{eV}$ <sup>[6]</sup>. At the same time, after Ti(II) sputtering for 600s, it was found that the spectrum at depth also contained these doublet as its Ti(II) and Ti(III) feature. The individual fitting parameters (binding energies  $E_b$  and the ratio  $r_i$  (%) =  $A_i / \sum A_i$ ) were listed in Table 1.

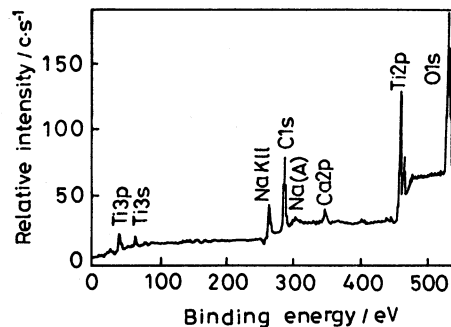
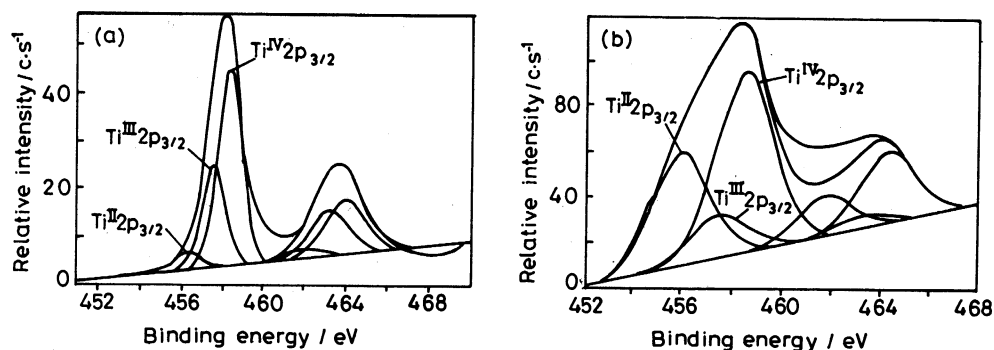


Fig.1 XPS survey spectrum for the surface of TiO<sub>2</sub> thin film



**Fig.2** XPS spectra of the Ti2p region: (a) on the surface and (b) at depth, after sputtering for 600s

**Table 1** Peak fitting results of the high resolution spectra of the Ti2p region.  $r_i$  (%) represents the ratio  $A_i/\sum A_i$  (relative contribution of each peak in a same sample)

		Ti <sup>IV</sup> 2p <sub>3/2</sub>	Ti <sup>IV</sup> 2p <sub>1/2</sub>	Ti <sup>III</sup> 2p <sub>3/2</sub>	Ti <sup>III</sup> 2p <sub>1/2</sub>	Ti <sup>II</sup> 2p <sub>3/2</sub>	Ti <sup>II</sup> 2p <sub>1/2</sub>
Surface	$E_b$ /eV	458.30	464.05	457.55	463.30	456.35	462.05
	$r_i$ /%	61.75	61.75	32.38	32.38	5.78	5.78
Sputtering 300s	$E_b$ /eV	458.55	464.35	457.55	463.35	456.20	462.35
	$r_i$ /%	60.83	60.83	11.88	11.88	27.29	27.29
Sputtering 600s	$E_b$ /eV	458.55	464.30	457.55	463.25	456.05	461.75
	$r_i$ /%	54.39	54.39	12.50	12.50	33.11	33.11

There are three possible causes of the titanium reduction process. The first one may be the presence of residual carbon in the layer from organic radicals introduced by molecular precursors. Carbon burnt and drew oxygen from the surrounding atmosphere and layer network during heat-treatment, which made Ti(IV) reduce to Ti(III), also a small amount of Ti(IV) and Ti(III) reduce to Ti(II). The second may be the sensitivity of Ti(IV) and Ti(III) ions towards the bombardment with argon ions where, according to the literature<sup>[5,7]</sup>, Ti(III) and Ti(IV) were easily reduced to Ti(II) as a result of the argon sputtering process. These results can be seen from Table 1. Therefore, the concentration of Ti(II) increased with depth, while that of Ti(III) and Ti(IV) decreased with depth. The third may be the diffusion of mobile sodium and calcium ions from the glass substrate, which caused bonding or a shift of the oxygen anions in the TiO<sub>2</sub> network. Naturally the process enabled Ti-O bond shortening and stimulated the reduction of Ti(IV) towards its lower valency state<sup>[7]</sup>.

**2.2.2 The O1s region** Fig.3(a,b) showed the high resolution XPS spectra of the O1s region, taken on the surface and at depth, after sputtering for 300s. The O1s region has been decomposed into several contributions. The results are presented in Table 2. For all the spectra taken on the surface and at depth, the main contribution can be attributed to TiO<sub>2</sub>. For the sample surface (see

Fig.3a), six oxygen contributions were taken into account: (a) from Ti-O bonds of TiO<sub>2</sub>, (b) from Ti-O bond of Ti<sub>2</sub>O<sub>3</sub>, (c) from Ti-O bonds of TiO, (d) from C-O bonds, (e) from hydroxyl groups and (f) from adsorbed H<sub>2</sub>O. As can be seen in Table 2 and Fig. 3(b), the last two contributions only appear in the spectrum on the surface, which can be attributed to H<sub>2</sub>O species easily adsorbed onto the surface of TiO<sub>2</sub> thin film, at the same time, also some H<sub>2</sub>O can react with TiO<sub>2</sub> to form Ti-OH, such as, H<sub>2</sub>O+Ti-O-Ti→2Ti-OH<sup>[2]</sup>. The C-O bonds were attributed to organic residue such as alcohol, unhydrolyzed alkoxide groups and CO<sub>3</sub><sup>2-</sup><sup>[9]</sup>.

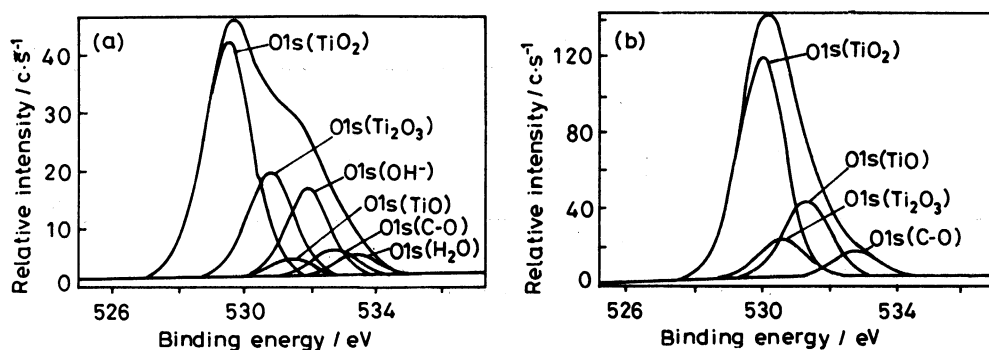


Fig.3 XPS spectra of the O1s region: (a) on the surface and (b) at depth, after sputtering for 300s

Table 2 Peak fitting results of the high resolution spectra of The Ti<sub>2p</sub> region.  $r_i$  (%) represents the ratio  $A_i/\sum A_i$  (relative contribution of each peak in a same sample)

		O1s(TiO <sub>2</sub> )	O1s(Ti <sub>2</sub> O <sub>3</sub> )	O1s(TiO)	O1s(OH <sup>-</sup> )	O1s(C-O)	O1s(H <sub>2</sub> O)
Surface	$E_b/eV$	529.45	530.80	531.40	531.90	532.80	533.40
	$r_i/\%$	49.43	21.41	3.36	16.82	5.05	3.93
Sputtering 300s	$E_b/eV$	529.95	530.60	531.35		532.80	
	$r_i/\%$	61.26	10.73	21.15		6.86	
Sputtering 600s	$E_b/eV$	529.93	530.65	531.20		532.80	
	$r_i/\%$	55.07	10.14	24.88		9.90	

### 2.3 Composition of the TiO<sub>2</sub> thin film

The compositions of the gel film initially obtained from the moment of the dipping process of the glass substrate, up to its final transformation in a solid oxide film, were perpetually changed during the course of heat-treatment. At first, hydrolysis-condensation reactions took place, and freeing alcoholic groups and introducing hydroxyl groups into the media. As drying begins, alcohol and water included in the gel volume as well as some of the as yet unreacted organometallic components evaporate. Drying and burning leading to a densification of the films were often accompanied by additional structural alterations, for example, the formation of new chemical bonds, the breaking of bonds, sublimation of some easily volatile components, immiscibility or

crystallization processes and so on. To a greater extent, the final composition of the films depended not only on the chemical composition of the sol solution but also on the intensity of hydrolysis and polycondensation processes, and on the substrates<sup>[7]</sup>.

On the basis of the phenomena described, it is clear that all parameters will extensively influence the composition, and hence the physical and chemical properties of the film itself. To perform a more adequate interpretation of the film properties, it was necessary to check the quantitative composition of the films on the surface and at depth. Analyses were carried out using the primary information from XPS<sup>[7]</sup>. The results were presented in Table 3.

**Table 3** Composition (atom percentage/%) of TiO<sub>2</sub> thin film according to XPS analyses

	Ti	O	C <sup>a</sup>	Na <sup>b</sup>	Ca <sup>b</sup>
Surface	15.38	32.86	43.39	5.83	2.54
Sputtering 300 s	36.00	52.30	8.84	2.32	0.54
Sputtering 600 s	35.07	53.39	8.71	2.25	0.58

a. elements introduced in the sol solution with the starting materials, which have subtracted the composition of contamination C from XPS instrument itself.

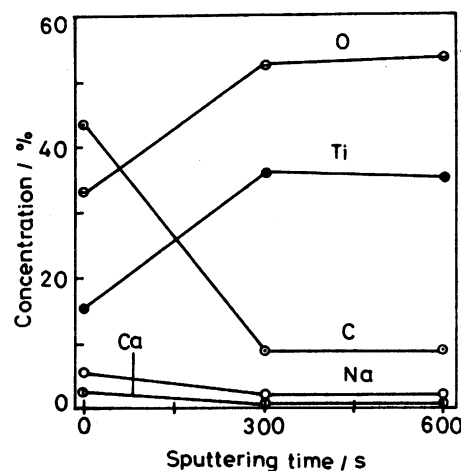
b. elements diffused from the glass substrate

It can be seen from Table 3 that the thermal diffusion of sodium and calcium ions from the substrate towards the TiO<sub>2</sub> thin film was an easily accomplished process. The sodium and calcium content in deep layers decreased. This was due to the argon-ion bombardment. Because sodium and calcium are light elements and possess high coefficients of sputtering<sup>[5]</sup>, they are easily sputtered and their concentrations were low in the interior of TiO<sub>2</sub> thin film. The carbon content on the surface was much larger than at depth, perhaps because carbon moves from the depth to the surface during heat-treatment.

Fig.4 showed that elements were comparatively uniformly distributed in depth. In the TiO<sub>2</sub> thin film, there were obvious increases in titanium and oxygen contents and decreases in the carbon, sodium and calcium concentrations from the surface to at depth.

### 3. Conclusions

In summary, besides oxides of Ti(IV) there was a certain amount of oxides of Ti(III) and Ti(II) in the sol-gel derived TiO<sub>2</sub> films. From the surface to the depth, titanium and oxygen contents



**Fig.4** Depth profile of the element concentration (atom percentage/%) of TiO<sub>2</sub> thin film

obviously increased, and the concentrations of carbon, sodium and calcium decreased. Elements were comparatively uniformly distributed in depth.

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