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Preparation and characterization of ZnO/TiO_2, $SO_4^{2-}/ZnO/TiO_2$ photocatalyst and their photocatalysis

Shijun Liao*, Huang Donggen, Denghua Yu, Yunlan Su, Gaoqing Yuan

Department of Applied Chemistry, College of Science, South China University of Technology, Wushan, Guangzhou 510641, PR China

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Abstract

A novel binary oxide photocatalyst ZnO/TiO_2 was prepared by a new modified sol–gel method using citric acid as a complex reagent and its photocatalytic activity was investigated. The factors, such as the ratio of amount of doped zinc ion, the precursors, and the calcination temperature on the activities of ZnO/TiO_2 photocatalyst, were investigated. $SO_4^{2-}/ZnO/TiO_2$ was prepared by sulfating the dry gels of ZnO/TiO_2 with H_2SO_4 solution. It was showed that the addition of ZnO could enhance the activity significantly, and sulfating ZnO/TiO_2 with sulfuric acid resulted to dramatic enhancement, the degradation ratio of methyl orange could be up to 71.9%, compared with 55% of degradation of ZnO/TiO_2 catalyst.

Keywords: ZnO/TiO_2 photocatalyst; Sol–gel method; Sulfating; Photocatalysis

1. Introduction

Titanium dioxide is acknowledged as the most important photocatalyst since it has many advantages to other materials, such as its high activities, lower prices and property of tolerating chemical and photo corrosions. One of the disadvantages of this catalyst is that its activity is still not high enough to be suitable for commercial application.

In order to enhance the activity of catalyst, many efforts have been paid to modify TiO_2 by adding some transition metals, such as Fe^{3+}, Mo^{6+}, La^{3+}, Gd^{3+}, W^{6+}, in the past two decades. Choi et al. [1] investigated the promotion of 21 types of transition metal on TiO_2 systemically, and suggested the relationship of photocatalysis of modified TiO_2 with holes and electrons generated by illumination. Anpo and Chiba [2] also reported that a titanium–silicon binary oxide was highly active as a photocatalyst in photocatalytic reactions of alkenes and alkynes with water. Do et al. [3], Papp et al. [4] and Fu et al. [5] have published results on TiO_2/WO_3, TiO_2/MO_3, TiO_2/SiO_2, and TiO_2/ZrO_2 systems. They found the degradation rates of volatile organic compounds over these binary metal oxides were enhanced. They also found a correlation between the enhanced photoreactivity and a higher surface acidity resulting from the addition of metal oxides. The surface acidity was thought to take the form of stronger surface hydroxyl groups, which accept holes generated by illumination and oxidize adsorbed molecules. These results suggest that binary oxides are potentially useful photocatalysts. Modifying TiO_2 by adding some hetero elements is viewed as one of the most important ways to explore novel photocatalyst.

In this contribution, a binary oxide catalyst TiO_2/ZnO was prepared by a new modified sol–gel method and the enhanced photocatalytic performance of ZnO doped TiO_2 was demonstrated. The photocatalytic activity and acidity of $SO_4^{2-}/TiO_2/ZnO$ modified by sulfating treatment were studied, which showed a better photocatalytic performance than pure TiO_2/ZnO. The crystal structure and surface property of ZnO/TiO_2 and $SO_4^{2-}/ZnO/TiO_2$ catalysts were also characterized by XRD, BET, and XPS techniques.

2. Experimental

2.1. Preparation of catalyst

All chemicals were analytical grade and used without further purification. 3.4 ml *n*-butyl titanate was dissolved into 18 ml anhydrate ethanol. Citric acid, precursor of zinc, water, and polyglycol were added successively at room temperature. The mixture was stirred for an hour. A light yel-

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* Corresponding author. Tel.: +86 2087114655; fax: +86 2087112906.
E-mail address: chsjliao@scut.edu.cn (S. Liao).

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low sol was obtained, aging for 24 h at room temperature and followed by drying at 80 °C for 48 h and pre-treating at 200 °C for 1 h. The obtained dry gel powder was ground and followed by calcining at various temperatures. A series of binary oxide catalyst, in which the zinc concentration is different, was prepared.

$SO_4^{2-}/ZnO/TiO_2$ catalyst was prepared by sulfating the dry gel after pretreatment at 200 °C or powders after calcination of ZnO/TiO_2 with $0.5\,mol\,l^{-1}$ H_2SO_4 solution.

2.2. *Characterization of the catalyst*

The XRD pattern was obtained at room temperature with a computerized Shimadzu XD-3A Diffractometer using Ni-filtered Cu Kα radiation. The measurements were carried out at 30 kV tube voltage and 30 mA current.

The surface area of the samples was measured by N_2 adsorption at 77 K using the dynamic BET method using a Zeton Altamira (Model AMI-200) sorptometer. The samples were purged in a He atmosphere at 473 K for an hour prior to adsorption.

X-ray photoelectron spectroscopy (XPS) was recorded with the PHI1600 Quantum ESCA Microprobe System, using the Mg Kα line of a 300 W Mg X-ray tube as a radiation source at 15 kV voltages. As an internal reference for the absolute binding energies, the C1s peak at 284.6 eV of the contaminated surface carbon was used. The fitting results of XPS curves were analyzed with a curve fitting software.

2.3. *Evaluation of photocatalytic activity of catalyst*

Methyl orange dye was used as reactant, the concentration was in the range of $0.1–1\,g\,l^{-1}$, the reaction was carried out in a 250 ml beaker with an electromagnetic stirrer, a 160 W high pressure mercury bulb was used as light source, the used amount of catalyst was 1 g for 100 ml solution, and the reaction time was 5 h. The concentration of methyl orange before and after reaction was measured by its absorbency at 474 nm wavelength with a 721 Spectrophotometer made in Shanghai, China. The degradation of reactant could be calculated by $D\ (\%) = 100(A_0 - A)/A_0$.

2.4. *Measurement of acidity of $SO_4^{2-}/TiO_2/ZnO$*

The acid strength was measured by indicator method in a lab-made vacuum measurement system. The sample was pretreated by vacuuming, heating, and cooling down to room temperature and introducing alkaline indicator vapor. The acid strength could be determined by observing the color change of sample before and after adsorption of indicator.

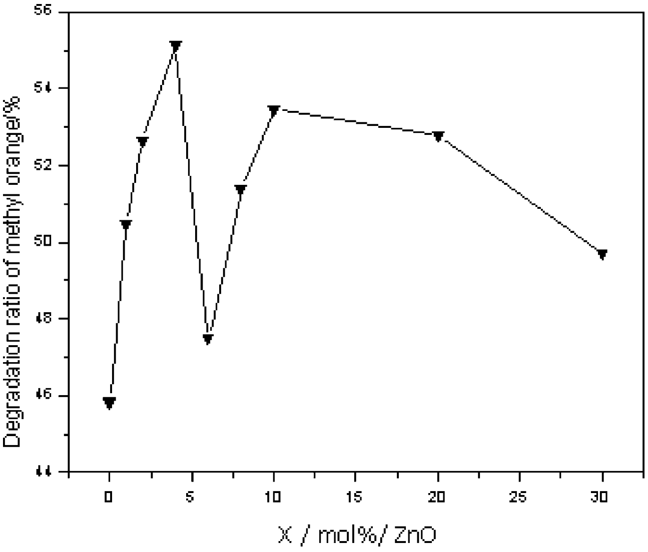

Fig. 1. Effect of the concentration of ZnO on the activity of ZnO/TiO_2.

3. Results and discussions

3.1. *Effect of adding amount of zinc oxide on the activity of ZnO/TiO_2 catalyst*

As shown in Fig. 1, the addition of zinc could enhance the activity of catalyst significantly, and the maximal activity is appeared at 4% of zinc concentration. This result may also be elucidated by XRD spectra shown in Fig. 2. It could be found that the sample of containing 4% zinc was a mixture of anatase and rutile and for other samples only the diffraction peaks of anatase titanium dioxide could be observed. Some researchers [6] also mentioned that a mixture of anatase and rutile TiO_2 could show better performance. The possible reason was that the anatase crystal combined

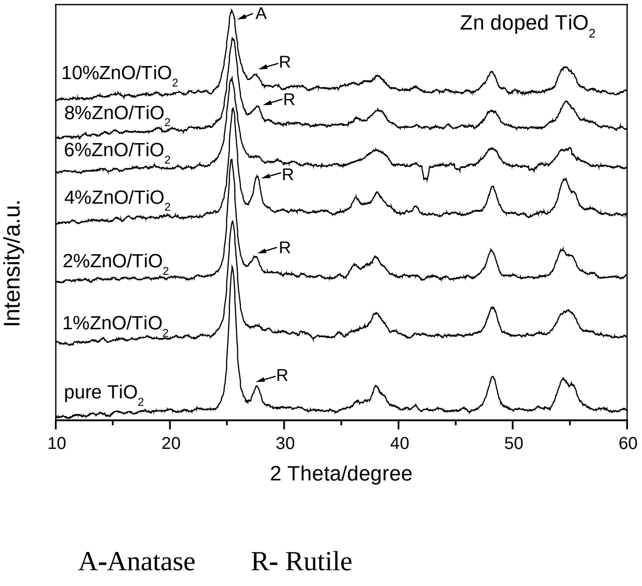

Fig. 2. XRD patterns of ZnO/TiO_2 (400 °C, 4 h) with different ZnO content.

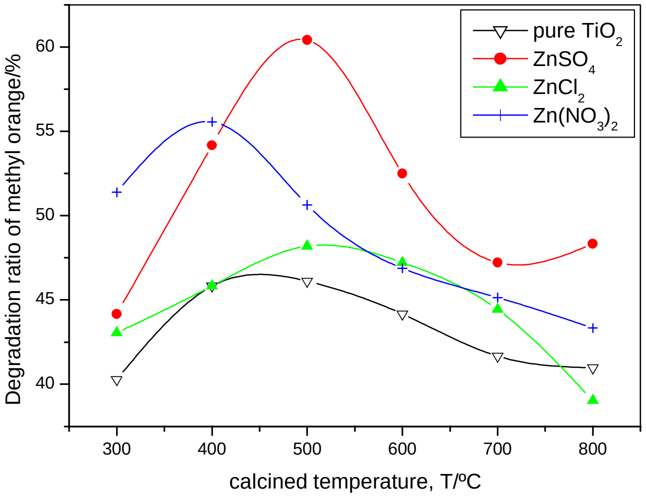

Fig. 3. Photocatalytic activities of 10% ZnO/TiO_2 catalysts calcined at different temperature by zinc sulfate, zinc nitrate and zinc chloride, respectively.

with little rutile phase could promote the separation efficiency of photo-generated electron and hole and improved the photocatalysis.

3.2. *Effects of precursor on the activity of ZnO/TiO_2 catalyst*

Some zinc containing materials, including zinc chloride, zinc nitrate, zinc sulfate, were used as the precursors of zinc, and it was found that the catalyst with zinc sulfate as precursor of zinc showed the best activity (Fig. 3). We speculate that it may be related with the existence of $SO_4{}^{2-}$ group. And it was verified by the fact that sulfating of the binary oxide catalyst treated with dilute H_2SO_4 solution could enhance the activity of catalyst remarkably, which is discussed in Section 3.5.

It was found that the calcining temperature was a very important factor affecting the activity. When zinc sulfate was used as precursor, the best calcining temperature was about 500 °C, and for zinc nitrate, the best calcining temperatures was 400 °C.

3.3. *The effect of the calcining temperature on the structure of ZnO/TiO_2 and $SO_4{}^{2-}$/ZnO/TiO_2*

The photoreactivities of the dry gel or powder of 10% ZnO/TiO_2 before and after sulfating at different calcining temperature are shown in Fig. 4. The photocatalytic activity of $SO_4{}^{2-}$/ZnO/TiO_2 was higher than that of ZnO/TiO_2 at the same temperature. The photocatalytic activity of $SO_4{}^{2-}$/ZnO/TiO_2 reached the maximum 63.19% at 550 °C with the increase of calcining temperature and decreased rapidly at 700 °C with further increase in temperature. The possible reason was that the interaction between $SO_4{}^{2-}$ and TiO_2 was strongest at 550 °C. With the increasing temperature, the photocatalytic activity decreased resulting from the decomposition of $SO_4{}^{2-}$on the one hand and the increase of the content of rutile and the appearance of impurity of $ZnTiO_3$ on the other hand, which was proved by the XRD results shown in Fig. 5.

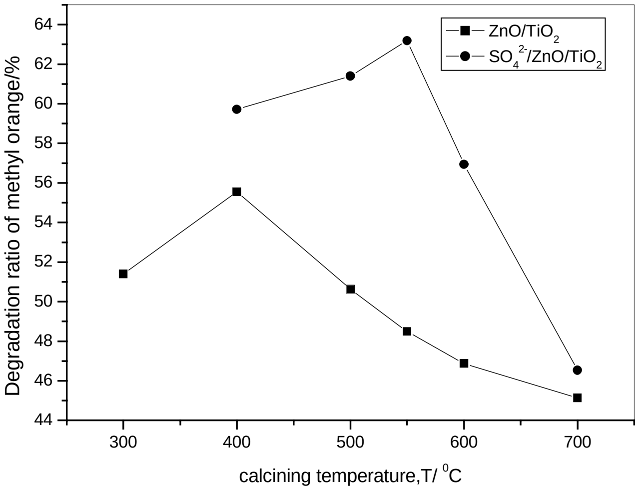

Fig. 4. Photocatalytic activities of ZnO/TiO_2 and $SO_4{}^{2-}$/ZnO/TiO_2 calcined at different temperature.

According to Fig. 5(a), with the increase of calcining temperature, the phase of TiO_2 in the catalyst would change from anatase ($2\theta = 25.4°$) to rutile ($2\theta = 27.5°$) and react with zinc salt to produce the impurity of $ZnTiO_3$ in all probability.

As shown in Fig. 5(b), the main crystal phase was still composed of anatase when the dry gel was treated with H_2SO_4 calcined at 700 °C. The existence of $SO_4{}^{2-}$ had the effect of stabilizing the anatase phase, restraining the phase change of TiO_2 and postponing the phase temperature of changing to rutile completely.

3.4. *Filtering/washing effect on the activity of $SO_4{}^{2-}$/ZnO/TiO_2*

The photocatalytic activities of $SO_4{}^{2-}$/ZnO/TiO_2, which was obtained from 10% ZnO/TiO_2 (400 °C, 4 h) impregnated with H_2SO_4 and followed by filtration, washing, desiccation and calcination at 550 °C for 4 h, are shown in Table 1. The sample treated by unfiltered, desiccated directly and calcined, showed the best photocatalytic catalysis. The amount of water for filtration and washing had a remarkable effect

Table 1
Influence of the amount of washing-water on the photocatalytic activities of $SO_4{}^{2-}$/ZnO/TiO_2 (10% ZnO) catalysts

The condition of filtration and washing after impregnation with H_2SO_4	Degradation ratio of methyl orange *D* (%)
Unfiltered	71.97
Filtered and washed by 50 ml water	52.78
Filtered and washed by 75 ml water	58.33
Filtered and washed by 100 ml water	57.64
Filtered and washed by 150 ml water	55.56
Filtered and washed by 200 ml water	51.39

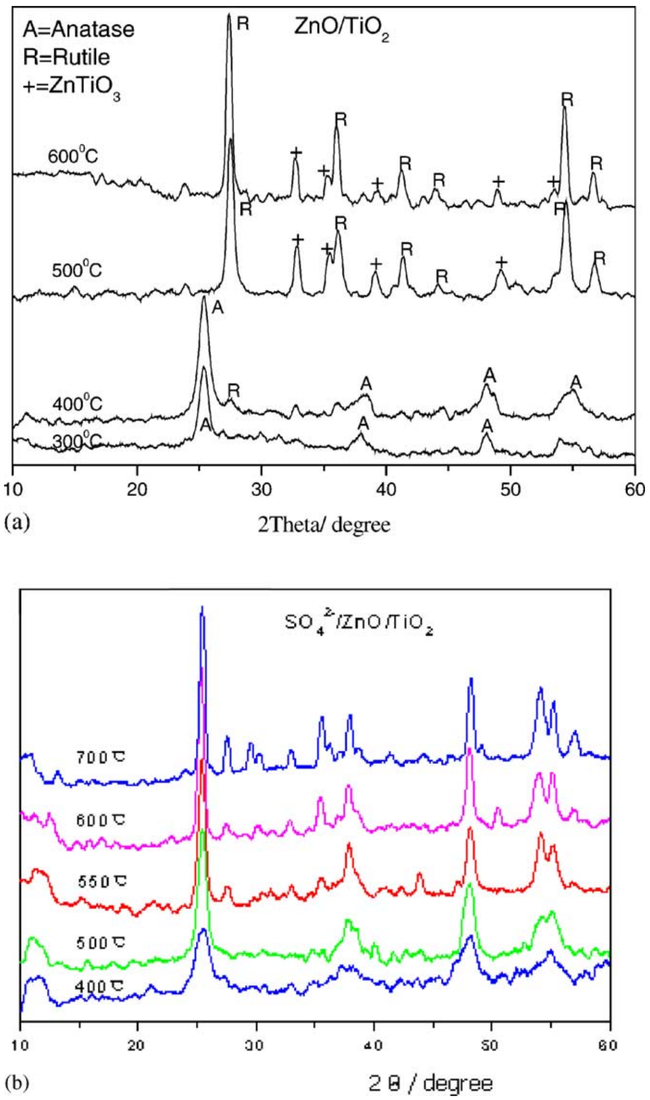

Fig. 5. (a) XRD patterns of 10% ZnO/TiO_2 by $Zn(NO_3)_2$ as precursor. (b) XRD patterns of SO_4^{2-}/ZnO/TiO_2 calcined at different temperature for 4 h.

on the activity of the catalyst, of which the best amount was 75 ml. This may be because of the loss of SO_4^{2-} and ZnO dissolved by H_2SO_4 in the process of washing.

3.5. Sulfating treatment on the activity of SO_4^{2-}/ZnO/TiO_2

The comparisons of photocatalytic activities of several catalysts before and after sulfating are shown in Fig. 6. The sulfating treatment was processed by powder impregnated with H_2SO_4, unfiltered, desiccated directly and calcined at 550 °C. The photocatalytic activities were improved markedly after sulfating. The catalytic activity of ZnO/TiO_2 (400 °C, 4 h) improved nearly 30%. The catalytic activity of self-made pure TiO_2 (400 °C, 4 h) treated with H_2SO_4 improved 24%. The activity of SO_4^{2-}/TiO_2 was little higher than that of ZnO/TiO_2. The activity of SO_4^{2-}/ZnO/TiO_2 was higher than that of TiO_2 doped by single ZnO or TiO_2 treated with single H_2SO_4. It can be seen that the higher photocatalytic activity of SO_4^{2-}/ZnO/TiO_2 results from the co-interaction of adulteration of ZnO and sulfating.

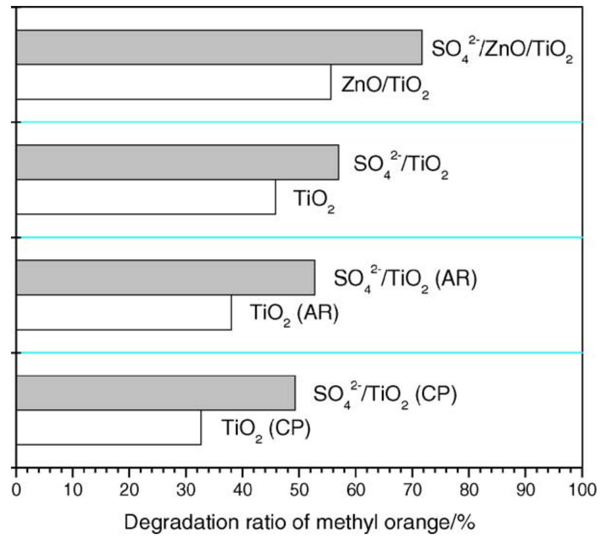

Fig. 6. Photocatalytic activities of several catalysts before and after treated with 0.5 mol l^{-1} H_2SO_4 solution.

3.6. BET method to determine the specific surface area

The specific surface areas of the catalyst before and after sulfating treatment are shown in Table 2. The adulteration of ZnO had no effect on the specific surface area of TiO_2. The specific surface area of the catalyst treated with H_2SO_4 was higher than that of the catalyst untreated with H_2SO_4, which was consistent with the literature [7]. The existence of SO_4^{2-} could prevent the growth of the crystal of catalyst. The specific surface area of the dry gel of 10% ZnO/TiO_2 (calcined at 400 °C for 4 h) after sulfating did not improve and was affected greatly by the concentration of H_2SO_4. Only when the concentration of H_2SO_4 was 0.5 mol l^{-1}, the specific surface area improved slightly, possibly because the dissolution of ZnO dispersed on the surface of TiO_2 destroyed the exterior structure of the catalyst and resulted in the decrease of specific surface area when ZnO/TiO_2 (400 °C, 4 h) was impregnated with H_2SO_4.

3.7. XPS analysis

The XPS results of 10% ZnO/TiO_2 (400 °C, 4 h) and SO_4^{2-}/10% ZnO/TiO_2 (550 °C, 4 h) are shown in Figs. 7 and 8. The main elements were Ti, Zn, O, and C before sulfating and Ti, Zn, O, C, S, and N after sulfating. Among them the element of C came from the pollution of the instrument and the element of N appearing after sulfating came from the un-decomposed nitrate dissolved by H_2SO_4. The content and binding energy of all elements in the surface of the catalyst before and after sulfating are shown in Table 3.

Table 2
BET surface area results of various catalyst samples

Catalyst sample	The specific surface area S_{BET} ($\mathrm{m^2\,g^{-1}}$)
Pure TiO_2 (400 °C, 4 h)	31.7
10% ZnO/TiO_2 (400 °C, 4 h)	32.6
10% ZnO/TiO_2 (400 °C, 4 h) impregnated by 0.1 $\mathrm{mol\,l^{-1}}$ H_2SO_4 for 1 h, unfiltered, desiccated directly and calcined at 550 °C for 4 h	21.0
10% ZnO/TiO_2 (400 °C, 4 h) impregnated by 0.3 $\mathrm{mol\,l^{-1}}$ H_2SO_4 for 1 h, unfiltered, desiccated directly and calcined at 550 °C for 4 h	30.6
10% ZnO/TiO_2 (400 °C, 4 h) impregnated by 0.5 $\mathrm{mol\,l^{-1}}$ H_2SO_4 for 1 h, unfiltered, desiccated directly and calcined at 550 °C for 4 h	34.6
10% ZnO/TiO_2 (400 °C, 4 h) impregnated by 1.0 $\mathrm{mol\,l^{-1}}$ H_2SO_4 for 1 h, unfiltered, desiccated directly and calcined at 550 °C for 4 h	18.9
10% ZnO/TiO_2 dry gel impregnated by 0.5 $\mathrm{mol\,l^{-1}}$ H_2SO_4 for 1 h, unfiltered, desiccated directly and calcined at 550 °C for 4 h	40.5

According to the table, the binding energy of Ti2p is 458 eV and S2p is 168.96 eV, which showed that Ti was in the form of Ti^{4+} and S was in the form of $SO_4{}^{2-}$ [8], which provided the probability of formation of super acid. The binding energy of Ti2p after sulfating increased appreciably, which showed that the positron of Ti^{4+} in the surface of the catalyst increased after sulfating. The change of the chemical state may increase the ability of oxygen adsorption and decrease the complex rate of photo-generated electron and hole [9].

The high resolution XPS of O1s in the surface of the catalyst before and after sulfating are shown in Table 4. The peak of O1s was broken up two peaks, corresponding to Ti–O of TiO_2 and hydroxyl group in the surface of the catalyst [10], respectively. The curve fit result of O1s are listed in Table 4. According to Fig. 9 and Table 4, the content of the hydroxyl group was higher after sulfating than before sulfating. The surface hydroxyl group came from the chemical adsorption of H_2O reacting with TiO_2 to form Ti–OH. Because the physical adsorption of H_2O existing in the surface of the catalyst was easy to desorption in the super high vacuum of XPS system, it did not appear in the spectrum of XPS. The atomic percentage of hydroxyl in the catalyst was obtained from the contribution value of O1s multiplying the atomic percent of O1s in the surface of catalyst. The hydroxyl group of $SO_4{}^{2-}/ZnO/TiO_2$ was 29.34%, which was 2.2 times than that of ZnO/TiO_2 (13.14%). In general, the abundant hydroxyl group in the surface of the catalyst did favor for the photocatalysis [11].

3.8. The acidity of $SO_4{}^{2-}/ZnO/TiO_2$

As shown in Table 5, the change of color of three adsorbed indicators could be observed on $SO_4{}^{2-}/TiO_2$ and $SO_4{}^{2-}$/10% ZnO/TiO_2 (the second method), showing that

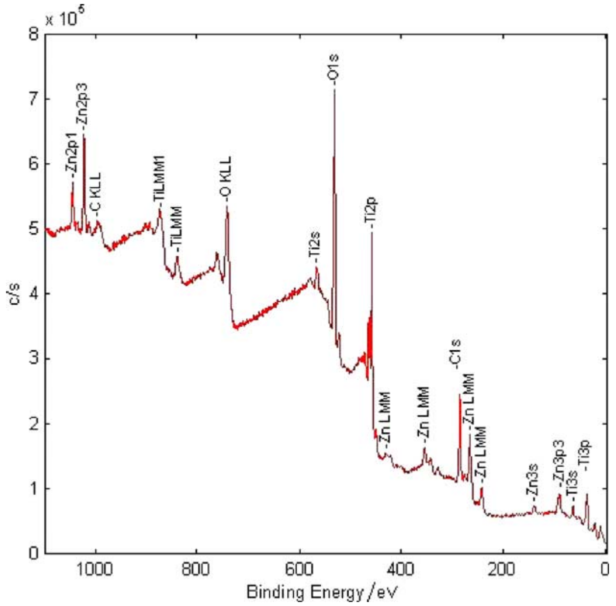

Fig. 7. XPS spectrum of the 10% ZnO/TiO_2 calcined at 400 °C for 4 h.

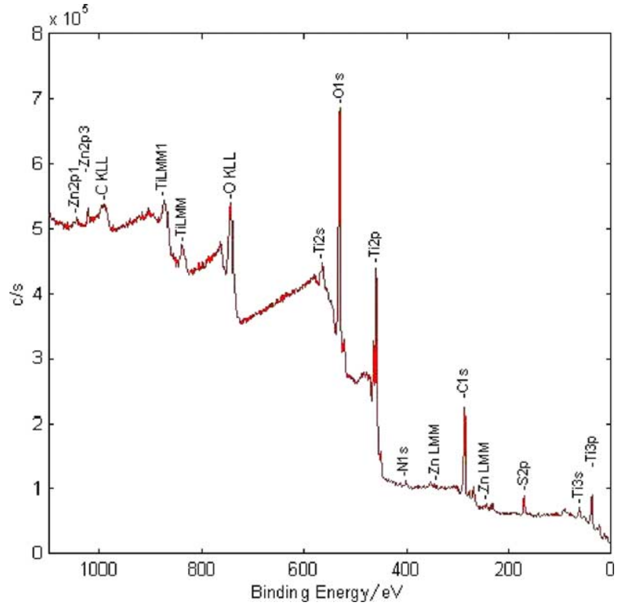

Fig. 8. XPS spectrum of the $SO_4{}^{2-}$/10% ZnO/TiO_2 calcined at 550 °C for 4 h by the 10% ZnO/TiO_2 (400 °C, 4 h) impregnated with 0.5 $\mathrm{mol\,l^{-1}}$ H_2SO_4 solution for 1 h.

Table 3
Composition (at.%) and binding energy of 10% ZnO/TiO_2 (400 °C, 4 h) before and after sulfating by XPS analyses

Catalyst		Ti2p	O1s	C1s	Zn2p	S2p	N1s
ZnO/TiO_2	at.%	18.2	51.4	12.9	17.4		
	E_b (eV)	458.38	529.64	284.59	1021.74		
$SO_4^{2-}/ZnO/TiO_2$	at.%	17.0	61.8	13.5	1.9	4.1	1.7
	E_b (eV)	458.71	529.97	284.55	1022.50	168.96	399.63

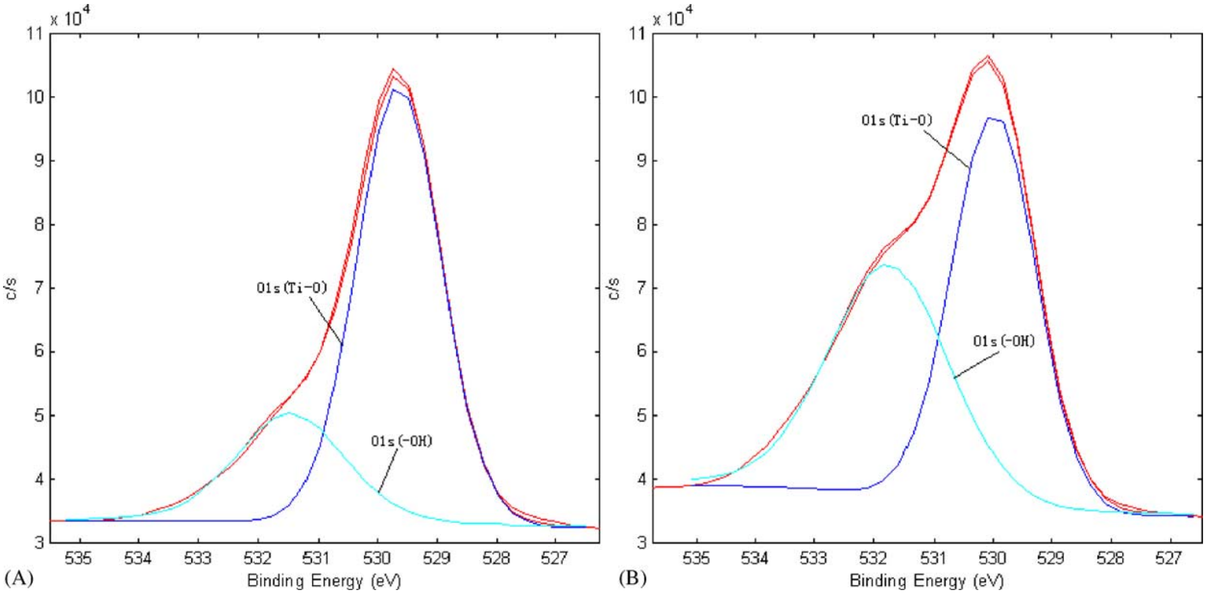

Fig. 9. High resolution XPS spectra of the O1s region for the surface of ZnO/TiO_2 catalyst before (A) and after (B) treatment with 0.5 M H_2SO_4 solution.

Table 4
Curve fitting result of high resolution XPS spectra for the O1s region

Catalyst sample		O1s (Ti–O)	O1s (–OH)
ZnO/TiO_2	E_b (eV)	529.64	531.46
	r_i (%)[a]	74.43	25.57
$SO_4^{2-}/ZnO/TiO_2$	E_b (eV)	529.97	531.76
	r_i (%)	52.52	47.48

[a] r_i (%) represents the ratio $A_i/\Sigma A_i$ (A_i is the area of each peak).

Table 5
Acid strength of SO_4^{2-}/TiO_2 and $SO_4^{2-}/ZnO/TiO_2$ (10% ZnO) catalyst samples

Indicator (H_0)	SO_4^{2-}/TiO_2	$SO_4^{2-}/ZnO/TiO_2$		
		(1)	(2)	(3)
p-Nitrotoluene (−11.35)	+	−	+	±
Nitrobenzene (−12.14)	+	−	+	−
2,4-Dinitrotoluene (−13.75)	±	−	+	−

+: color changed clearly; ±: color changed unclearly; −: color was unchanged. (1) 10% ZnO/TiO_2 dry gel impregnated by H_2SO_4 and unfiltered; (2) ZnO/TiO_2 (400 °C, 4 h) impregnated by H_2SO_4 and unfiltered; (3) ZnO/TiO_2 (400 °C, 4 h) impregnated by H_2SO_4, filtered and washed by 75 ml water.

they were super acid and their acidity achieved −13.75. The first and third methods of treating 10% ZnO/TiO_2 could not make three indicators change colors at all, showing that they did not possess the property of super acid. Different sulfating treatment resulted in the difference of acidity of SO_4^{2-}/10% ZnO/TiO_2, mainly because of the content of SO_4^{2-}. Comparing the acidity of SO_4^{2-}/10% ZnO/TiO_2 (2) and (3) (Table 5) with Table 1, it was found that the stronger the acidity, the higher was the catalytic activity. This was because the increase of surface acidity favor for the transfer of photo-generated electron in conduction band to the surface, resulting in the improvement of the separation efficiency of electron–hole and the progress of photoreaction [12].

Acknowledgements

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