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Effect of surface state properties of modified TiO_2 powders on their photo-catalytic activity①

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[Abstract] With an attempt to investigate the effect of gold impurity and tungsten oxide on the recombination and separation of electron-hole pairs, and disclose the effect of surface state on the photo-catalytic activity of TiO_2, an innovative photo-catalyst 3% WO_3/0.5% Au^{3+}/TiO_2 was prepared by means of sol-gel method. The photo-oxidation efficiency of photo-catalyst was evaluated by conducting a set of experiments to photo-degrade methylene blue (MB) in aqueous solution. The surface state properties were examined by means of surface photovoltage spectra (SPS) and electron-field-induced SPS (EFISPS). The experiments demonstrate that the strongest peak is attributed to electron excited from valence band to conduction band and the second strongest peak is attributed to electron excited from valence band to oxygen molecular for all samples. Electron is trapped by O_2 absorbed on the surface of TiO_2. And the surface state of O_2^- forms. For (1%, 3%) Au^{3+}/TiO_2 sample, two new peaks that significantly present at 414 nm and 400 nm respectively should be attributable to gold impurity energy level. And for tungsten oxides doping samples, 4 peaks that significantly present in the region of 500~ 800 nm should be attributable to tungsten impurity energy level. The intensity of EFISPS decreases with increasing the content of gold ion or tungsten oxide when its content is no more than their optimal dosage. However, when the content of gold ion or tungsten oxide is more than their optimal dosage, impurity energy level becomes recombination center from separation center and the intensity of all peaks increases for them.

[Key words] surface state; titanium dioxide; tungsten oxide; surface photovoltage spectra; methylene blue; gold ion
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1 INTRODUCTION

TiO_2 photo-catalysis has been the focus of numerous investigations in recent years, particularly owing to its application for the complete mineralization of undesirable organic contaminants to CO_2, H_2O and inorganic constituent[1]. However, photo-oxidation was almost not industrially applied to treat waste water due to its low reaction rate[2]. The higher recombination rate of electron/hole pairs limits the rate of photo-oxidation of organic compounds on the surface of a catalyst[3]. Numerous investigation have reported that the additions of group Ⅷ metals and transition metal ions to TiO_2-based photo-catalytic systems are two effective ways to enhance the photo-catalytic reaction rate[3, 4]. Choi and co-workers[5] presented the results of a systematic study of the effects of 21 different metal ion (not including gold ion) dopants on the photochemical reactivity of quantum-sized TiO_2 with respect to both chloroform oxidation and carbon tetrachloride reduction. Enhanced photo-activity was found for Fe^{3+}, Mo^{5+}, Ru^{4+}, Re^{5+}, V^{4+}, and Rh^{3+} substitution for Ti^{4+} at 0.5% molar level in the TiO_2 matrix. There are a number of studies related to the photocatalytic activity of metal oxide-TiO_2 catalysts for the purpose of improving TiO_2 photocatalytic activity, including Fe_3O_4[6], Sb_2O_3[7], WO_3[8~10], SiO_2[11], and Y_2O_3[12].

At meantime, a number of literatures were related to the interaction between the impurity and the support, and explored the mechanism of the enhancement of photo-activity of metal oxide-TiO_2 or metal ion-TiO_2. UPS, XPS and AES techniques have provided evidence for electron transfer from the support to the metal or metal ion[9, 13]. Zhang et al[14] proposed the existence of impurity energy level in the lattice of metal ion-TiO_2 by powder conductivity technique. Substitutional impurities such as V, Cr, Mn and Fe were doped in single crystalline rutile TiO_2 and the impurity levels of them were investigated by photocurrent measurement and theoretical calculations[15, 16]. Several of papers dealt with the relation-

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ship between the recombination of electron/hole pairs and photo-degradation efficiency by means of photoluminescence spectroscopy. Fujihara et al[17] reported that the intensity of PL emission decreased and the increase of the quantum efficiency of 2-propanol photo-degradation due to the addition of Fe^{3+} ions in the system of TiO_2 aqueous solution. Recently, our group has investigated the effect of gold ion doping and WO_3 composite on the photo-catalytic activity of TiO_2[9, 13, 18]. In our investigation, an innovative catalyst, $WO_3/Au^{3+}/TiO_2$ was prepared and photo-voltage spectra will be applied to investigate the effect of gold impurity and tungsten oxide on the recombination and separation of electron-hole pairs, and to disclose the effect of surface state on the photo-catalytic activity of TiO_2.

2 EXPERIMENTAL

2.1 Preparation of photo-catalysts

Gold ion doped TiO_2 samples were prepared by sol-gel method[13, 19]. A 17 mL tetra-*n*-butyl titanium ($Ti(O\text{-}Bu)_4$) dissolved in 80 mL absolute ethanol was added drop-wise under vigorous stirring to 100 mL mixture solution containing 80 mL 95% ethanol, 5 mL 0.1 mol/L tetrachloroauric acid and 15 mL acetic acid. The resulting transparent colloidal suspension was stirred for 2 h and was aged for 2 days till the formation of gel. The gel was dried at 353K under vacuum and then ground. The powder was calcined at 973 K for 2 h, and then gold-doped TiO_2 was obtained in a nominal atomic doping level of 1.0%, and abbreviated as 1.0% Au^{3+}/TiO_2. Other gold-doped TiO_2 samples were prepared according to the above procedure. They were 0.5% Au^{3+}/TiO_2 and 2.0% Au^{3+}/TiO_2 respectively.

Sol-gel process was used to prepare WO_3/TiO_2 samples[9]. Firstly, 0.05 mol TiO_2 transparent sol was prepared, using $Ti(O\text{-}Bu)_4$, 120 mL absolute ethanol, 15 mL acetic acid, 5 mL double distilled water, aged for 1 day. Secondly, 3.0 mL water solution of ammonium tungstate $(NH_4)_{10}H_2W_{12}O_{42}\cdot 4H_2O$ was added drop-wise to the sol under vigorous stirring for 2 h. And WO_3/TiO_2 gel formed. WO_3/TiO_2 sample was obtained in a nominal atomic doping level of 1.5% after aged, dried, ground, and sintered at 973 K for 2 h, and abbreviated as 1.5% WO_3/TiO_2. (3%, 5%) WO_3/TiO_2 samples were prepared according to the above procedure.

Gold ion doped WO_3/TiO_2 samples were prepared as follows. A 17 mL tetra-*n*-butyl titanium ($Ti(O\text{-}Bu)_4$) dissolved in 80 mL absolute ethanol was added drop-wise under vigorous stirring to 100 mL mixture solution containing 80 mL 95% ethanol, 5 mL 0.1 mol/L tetrachloroauric acid and 15 mL acetic acid. The resulting transparent colloidal suspension was stirred for 2 h and aged for 12 days. Thereafter, 6.0 mL water solution of ammonium tungstate $(NH_4)_{10}H_2W_{12}O_{42}\cdot 4H_2O$ was added drop-wise to the sol under vigorous stirring for 2 h. The gel was dried at 353 K under vacuum and then ground. The powder was calcined at 973 K for 2 h, and then 3% WO_3/0.5 Au^{3+}/TiO_2 sample was obtained. All concentration mentioned in this work were the nominal atomic concentration, which was based upon the assumption of quantitative incorporation of WO_3. All chemicals in this work were of analytical grade, and double distilled water was used for solution preparation.

2.2 Characterization of photo-catalysts

Surface photo-voltage spectra (SPS) were obtained with a solid junction photovoltaic cell by a light source-monochromator-lock-in detection technique. Monochromatic light was obtained by passing light from a 500 W xenon lamp through a double prism monochromator. A lock-in amplifier, synchronized with a light chopper, was used to amplify the photo-voltage signal. The photo-voltages were normalized so that the intensities of monochromatic light incident on the surface of the samples were constant. Electron-field-induced SPS (EFISPS) were obtained by means of 2.0 V applied.

2.3 Photoreactor and light source

A 125 W high-pressure mercury lamp (Institute of Electric Light Source, Beijing) was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp, as described in Ref. [13]. Aqueous suspensions were prepared by adding 0.2 g photo-catalyst powder to a 165 mL of aqueous dye solution ($\rho(MB) = 12$ mg/L, MB is from The British Drug Houses LTD). Prior to irradiation the suspensions were magnetically stirred in the dark for 15 min to establish the adsorption/desorption equilibrium of dye. Aqueous suspensions containing dye were irradiated under constant aerating. At given irradiation time intervals, samples of the suspension were taken and immediately centrifuged at 4 200 r/min for 20 min, then filtered to remove the particles. The filtrates were analyzed. MB concentration was analyzed by the Spectronic Genesys-2 UV-visible spectroscopy at 664 nm[13].

3 RESULTS AND DISCUSSIONS

3.1 Surface photo-voltage spectra

The determination of the relationship between the surface photo-voltage of a material and wavelength can provide some information about the surface state and photo-sensitization of the materials. The photo-voltage response arises from the generation of electron/hole pairs by photo-excitation. Light absorp-

tion usually leads to a direct transition from the valence band to the conduction band, with the production of electron/hole pairs. However, the generation of a photo-voltage response is a direct result of the free carriers. Light absorption often causes exciton rather than free carriers. The excitons must dissociate into free carriers for the production of photo-voltage[20]. However, the self-established field of samples is weak, electric-field-induced surface photo-voltage spectroscopy (EFISPS) is applied to produce strong photo-voltage response in our investigation.

Fig. 1 shows the SPS of TiO_2, 1.5% WO_3/TiO_2 and 3% WO_3/0.5Au^{3+}/TiO_2. To illustrate the results in this figure, the position of peaks is listed in Table 1. The positive peaks at 336 nm for TiO_2 and at 340 nm for 1.5% WO_3/TiO_2 and at 343 nm for 3% WO_3/0.5Au^{3+}/TiO_2 are attributed to electron excited from valence band to conduction band. The response at 436 nm for 1.5% WO_3/TiO_2 may be attributable to electron excited from valence band to oxygen absorbed by this catalyst. The response for TiO_2 present at 389 nm, 568 nm and 577 nm, and small peaks at 555 nm, 595 nm, 650 nm and so on for 1.5% WO_3/TiO_2, and 563 nm, 629 nm for 3% WO_3/0.5Au^{3+}/TiO_2 may be attributable to impurity energy level or defect energy level[15, 16, 21, 22].

Fig. 2 and Table 1 show the EFISPS of photocatalysts. When a positive electric field (+2.0 V) was applied, photo-induced electrons diffuse to the surface and holes diffuse into the body[21, 22]. The peaks at 332 nm, 337 nm, 335 nm, 334 nm for TiO_2, and 0.5%, 1.0%, 2.0% Au^{3+}/TiO_2 respectively are attributed to electron excited from valence band to conduction band. The peak at 435 nm, 437 nm for TiO_2 and 0.5% Au^{3+}/TiO_2 respectively is attributed to electron excited from valence band to oxygen molecular. The position of this peak shifts to red direction owing to gold ion doping in comparison with that of TiO_2. Electron is trapped by O_2 absorbed on the surface of TiO_2. And the surface state of O_2^- forms. These results have an agreement with that reported by CAO et al[21, 22]. Only for 1.0% Au^{3+}/TiO_2 and 2.0% Au^{3+}/TiO_2, a new peak significantly presents at 414 nm and 400 nm respectively. These peaks should be attributable to gold impurity energy level.

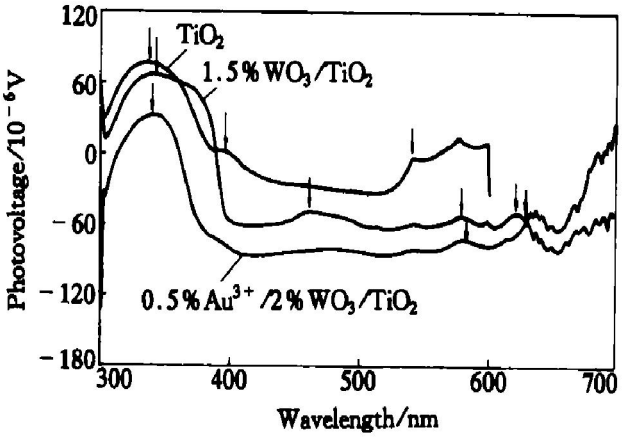

Fig. 1 SPS of photo-catalysts in range of 300~700 nm

EFISPS of WO_3/TiO_2 samples are showed in Fig. 3 and the peaks of EFISPS are listed in Table 1. The strongest peak is attributed to electron excited from valence band to conduction band, and the second strongest peak is attributed to electron excited

Table 1 Position of peaks of surface photo-voltage spectra (SPS) and electron-field-induced surface photo-voltage spectra(EFISPS) (nm)

Spectrum	Sample	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6
SPS	TiO_2	336	389	—	568	577	—
	1.5% WO_3/TiO_2	340	436	—	555	595	650
	3% WO_3/0.5% Au^{3+}/TiO_2	443	—	—	563		629
EFISPS	TiO_2	332	435	—	—	—	—
	1.5% WO_3/TiO_2	340	436	522	555	595	652
	3% WO_3/TiO_2	332	437	523	557	597	653
	5% WO_3/TiO_2	340	438	524	557	600	653
	0.5% Au^{3+}/TiO_2	337	437	—	—	—	—
	1.0% Au^{3+}/TiO_2	335	414	—	—	—	—
	2.0% Au^{3+}/TiO_2	334	400	—	—	—	—
	3% WO_3/0.5% Au^{3+}/TiO_2	331	437	525	557	600	653

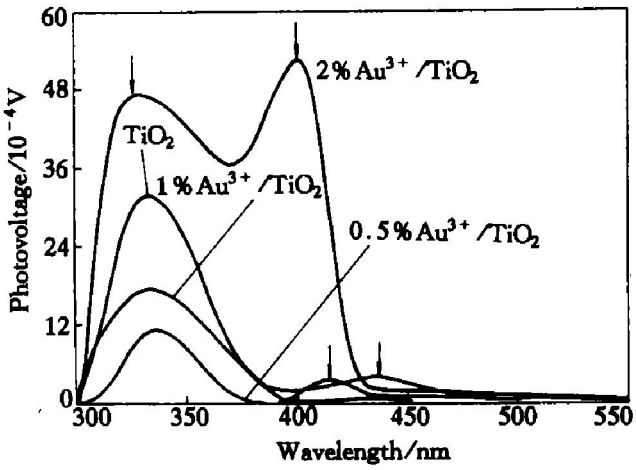

Fig. 2 EFISPS of Au^{3+} /TiO_2 in range of 300~ 700 nm

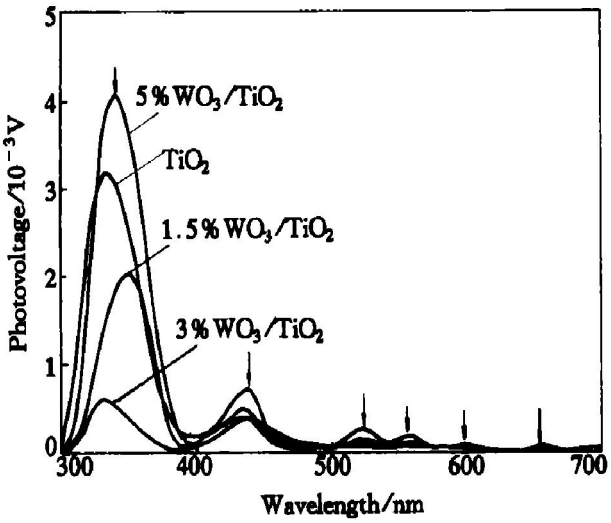

Fig. 3 EFISPS of WO_3/TiO_2 in range of 300~ 700 nm

from valence band to oxygen molecular for all samples. Electron is trapped by O_2 absorbed on the surface of TiO_2. And the surface state of O_2^- forms. These results have an agreement with that reported by CAO et al[21, 22]. Only for tungsten oxides doping samples, 4 peaks significantly present in the region of 500~ 800 nm. The position of all peaks shifts to red direction owing to tungsten oxides in comparison with that of TiO_2. The EFISPS peak attributable to electron excited from valence band to conduction band for WO_3 should not present in this region because its band gap is about 3.2 eV. So these peaks should be attributable to tungsten impurity energy level. EFISPS of 3% WO_3/0.5% Au^{3+} /TiO_2 sample is very similar to that of WO_3/TiO_2 samples, as described in Fig. 4.

3.2 Photocatalytic activity

For the purpose of comparison of photoactivity and the optimum dosage of gold ion and tungsten oxide, the photodegradation of MB dye was carried out. The photocatalytic activity was characterized by

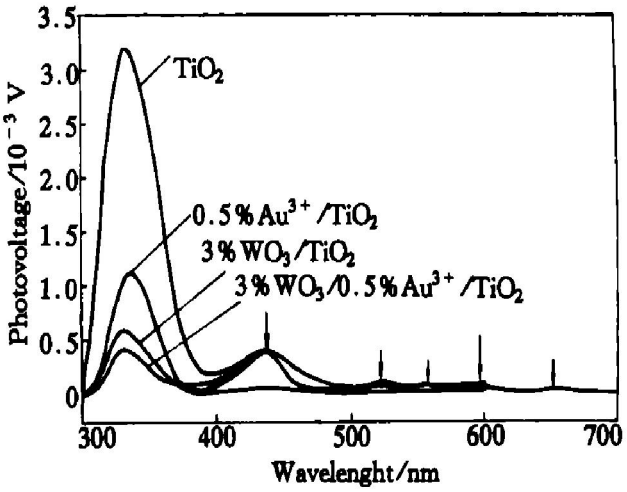

Fig. 4 EFISPS of photocatalysts in range of 300~ 700 nm

using pseudo-first-order kinetics with respect to MB concentration listed in Table 2. The observed photoactivity is low in the presence of pure TiO_2 and increased greatly with increasing the content of gold ion up to 0.5%, and decreased with increasing the content of gold ion. That implies there is an optimum molar content of gold ion, which is 0.5%. Similarly, the observed photoactivity of WO_3/TiO_2 is increased greatly with increasing the content of WO_3 up to 3%, and decreased with increasing the content of WO_3. This implies there is an optimum molar content of WO_3, which is 3%. And the photocatalytic activity of 3% WO_3/0.5% Au^{3+} /TiO_2 is strongest among all photocatalysts. The results show that WO_3 and gold ion should enhance the photocatalytic activity of TiO_2.

Table 2 Pseudo-first-order kinetics constants of MB (20 mg/L) in presence of modified TiO_2

Photocatalysts	Kinetics constant k/min^{-1}	Correlation coefficient, R^2
Pure TiO_2	0.095 5	0.996 1
1.5% WO_3/TiO_2	0.115	0.997 8
3.0% WO_3/TiO_2	0.166	0.999 2
5.0% WO_3/TiO_2	0.134	0.996 8
0.25% Au^{3+} /TiO_2	0.121	0.996 5
0.5% Au^{3+} /TiO_2	0.194 4	0.973 6
1.0% Au^{3+} /TiO_2	0.112	0.997 3
3.0% Au^{3+} /TiO_2	0.078 3	0.995 9
3% WO_3/0.5% Au^{3+} /TiO_2	0.213 6	0.998 6

3.3 Relationship between EFISPS and photocatalytic activity

The change of intensities of EFISPS can be explained from the conversion of excitons into separate electron/hole pairs. The electrons excited from the

valence band of TiO_2 will be trapped by surface oxygen and impurity, or will transfer to the conduction band. The electron/hole pairs are efficiently separated. The conversion from electrons excited to free carrier will be hindered. So, the intensity of EFISPS is decreased with increasing the content of gold ion or tungsten oxide when its content was no more than their optimal dosage. However, when the content of gold ion or tungsten oxide is more than their optimal dosage, impurity energy level becomes recombination center from separation center and the intensity of all peaks is increased for them. It deserves mentioning that the order of EFISPS intensity from weak to strong have a good agreement with that of PL intensity and that of photoactivity from strong to weak. So in this paper, the change of EFISPS is caused by the change of electron/hole pair recombination rate, and the photoactivity is greatly affected by the recombination rate.

[REFERENCES]

[1] Hoffmann M R, Martin S T, Choi W Y, et al. Environmental applications of semiconductor photocatalysis [J]. Chem Rev, 1995, 95: 69- 96.

[2] Goswami D Y. A review of engineering developments of aqueous phase solar photocatalytic detoxification and disinfection processes [J]. J Sol Energ-T ASME, 1997, 119(5): 101- 106.

[3] Linsebigler A, Lu G, Yates J T. Photocatalysis on the TiO_2 surfaces: principles, mechanisms, and selected results [J]. Chem Rev, 1995, 95: 735- 758.

[4] Yonezawa T, Matsune H, Kunitake T. Layered nanocomposite of close-packed gold nanoparticles and TiO_2 gel layers [J]. Chem Mater, 1999, 11: 33- 35.

[5] LI Xin-jun, LI Fang-bai, GU Guo-bang, et al. The preparation of nanometer-sized magnetic photocatalysts and their photocatalytic activity and properties [J]. The Chinese Journal of Nonferrous Metal, (in Chinese), 2001, 11(6): 971- 976.

[6] Choi W, Termin A, Hoffmann M R. The role of metal ion dopants in quantum-sized TiO_2: correlation between photoreactivity and charge carrier recombination dynamics [J]. J Phys Chem, 1994, 98: 13669- 13679.

[7] LI Fang-bai, GU Guo-bang, LI Xin-jun, et al. The enhanced photocatalytic behavior of Sb_2O_3/TiO_2 semiconductor nanopowder [J]. Chinese Journal of Inorganic Chemistry, (in Chinese), 2001, 17: 37- 42.

[8] Do Y R, Lee K, Dwight K, et al. The effect of WO_3 on the photocatalytic activity of TiO_2 [J]. J Solid State Chem, 1994, 108: 198.

[9] LI X J, LI F B, YANG C L, et al. Photocatalytic activity of WO_x-TiO_2 under visible light irradiation [J]. J Photochem & Photobio A, 2001, 141(2- 3): 209- 217.

[10] Alemany L J, Lietti L, Ferlazzo N, et al. Reactivity and physicochemical characterization of V_2O_5-WO_3/TiO_2 De-NO_x catalysts [J]. J Catal, 1995, 155: 117.

[11] Ramis G, Busca G, Cristiani C, et al. Characterization of tungsten-titania catalysts [J]. Langmuir, 1992, 8: 1744- 1749.

[12] LI Fang-bai, GU Guo-bang, LI Xin-jun, et al. Preparation, characterization and its photocatalytic behavior of Y_2O_3/TiO_2 composite semiconductor nanopowder [J]. Journal of Rare Earth, 2001, 19(3), 187- 191.

[13] LI X J, LI F B. Study of Au/Au^{3+}-TiO_2 photocatalysts toward visible photooxidation for water and waste water treatment [J]. Environ Sci & Technol, 2001, 35: 2381- 2387.

[14] ZHANG F L, ZHAO J C, SHEN T, et al. Applied Catalysis B: Environmental, 1998, 15: 147.

[15] Mizushima K, Tanaka M, Asai A, et al. Impurity levels of iron-group ions in TiO_2(Ⅱ) [J]. J Phys Chem Solids, 1979, 40: 1129- 1140.

[16] MO S D, LIN L B, LIN D L. Electron states of iron group impurities in doped rutile (TiO_2) [J]. J Phys Chem Solids, 1994, 55: 1309- 1313.

[17] Fujihara K, Izumi S, Ohno T. Time-resolved photoluminescence of particulate TiO_2 photocatalysts suspended in aqueous solutions [J]. J Photoch Photobio A, 2000, 132: 99- 104.

[18] LI Fang-bai, GU Guo-bang, LI Xin-jun, et al. The preparation, characterization and its photocatalytic behavior of WO_3/TiO_2 coupled semiconductor nanopowder [J]. Acta Physico-Chimica Sinica, (in Chinese), 2000, 16: 997- 1001.

[19] LI Fang-bai, GU Guo-bang, HUANG Guo-feng, et al. Enhanced photocatalytic activity of gold ion and gold modified TiO_2[J]. Journal of Environmental Sciences, 2001, 13(2): 201- 204.

[20] Kronik L, Shapira Y. Surface photovoltage phenomena: theory, experiment, and applications [J]. Surf Sci Rep, 1999, 37: 1- 206.

[21] CAO Y A, DING L, MA Y, et al. Effect of surface state properties of TiO_2 nanoparticle film on its photocatalytic activity [J]. Chem J Chin U, (in Chinese), 1999, 20: 1787- 1789.

[22] CAO Y A, XIE T F, ZHANG X T, et al. Investigation on surface state of TiO_2 nanoparticulate film [J]. Acta Phys-Chim Sin, (in Chinese), 1999, 15: 680- 683.

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