A visible-light response vanadium-doped titania nanocatalyst by sol–gel method

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Abstract

A series of vanadium-doped TiO_2 catalysts were synthesized by two modified sol–gel methods. V-doped TiO_2 was found to be mainly preserved its anatase phase after calcination at $400\,°C$. The TEM micrographs showed the sizes of primary particles were in the range of 6–20 nm. The increase of vanadium doping promoted the particle growth, and enhanced "red-shift" in the UV-Vis absorption spectra. The XPS (X-ray photoelectron spectroscopy) could not detect vanadium indicating negligible vanadium on the surface of catalysts, furthermore, there were also no peak of vanadium oxide in the XRD patterns. XAS (X-ray absorption spectroscopy) analysis indicating V^{4+} instead of V^{5+} implied that vanadium either substituted Ti^{4+} site or embedded in the vacancy of TiO_2 structure. Therefore, vanadium was concluded to be highly dispersed inside the TiO_2 structure. The photocatalytic activity was evaluated by the degradation of crystal violet (CV) and methylene blue (MB) under visible light irradiation. The degradation rate of CV and MB on V-doped TiO_2 were higher than those of pure TiO_2. As the results, V-doped TiO_2 possessed better absorption ability of visible light.

1. Introduction

Titania is a well-known photocatalyst. Many applications using titania in photo reactions have been successfully developed, such as the purification of contaminated water and the remediation of polluted air [1]. However, most applications so far are limited to UV light irradiation because the light absorption edge of pure titania is less than 380 nm. More than 96% solar light reaches earth surface is in the range of visible light (mostly 400–600 nm) since most UV is filtered by ozone layer. Therefore, a visible-light response photocatalyst becomes a recent trend in order to take full advantage of visible light. A few of visible-light photocatalysts were reported recently. Asahi et al. [2] reported a nitrogen doped titania possessed viable light photocatalytic activity in the photodegradation of methylene blue and acetaldehyde and its hydrophilicity. Anpo et al. [3] used ion implantation to dope a series of transition metal, such V, Cr and Ni into TiO_2 films with band gap shifting to visible light. Zhoa et al. [4] prepared a V/TiO_2 film and found an increase doping of vanadium resulting in further red-shift in UV-Vis spectroscopy. A series of transition metal were incorporated in

TiO_2 and tested by photoreaction under visible light by Choi et al. [5]. Klosek and Raffrey [6] deposited V on a TiO_2 film with dip coating technique, and obtained a monolayer vanadium, which was active using visible light (396–450 nm). In summary, vanadium doping provides a promising strategy to improve the photoactivity of titania under visible light.

The sol–gel process is one of the versatile methods to prepare nano-size materials. This technique does not require complicated instruments such as chemical vapor deposition. It provides a simple and easy means of synthesizing nano-size particles, which is essential for nano catalysts. The incorporation of an active metal in the sol during the gelation stage allows the metal to have a direct interaction with support, therefore the material posses special catalytic properties. One of the most promising photocatalysts for CO_2 photoreduction was supported copper titania which was previously synthesized using sol–gel method in our lab [7]. Although titania catalysts have been extensively studied, the procedure of preparing photocatalytic metal-doped titania are still of great interesting.

The research is aimed to develop a visible-light response catalyst via vanadium doping. The objective is to prepare a uniformly and highly dispersed state of the V^{4+} incorporated titania photocatalyst so that its electronic properties is modified, enabling the absorption of visible light [8].

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2. Experimental

2.1. Preparation of catalysts

Two methods were used to dope vanadium in TiO_2 catalyst. Fig. 1 illustrates the first modified sol–gel procedure. Vanadyl acetylacetonate was completely dissolved in the n-butanol solution. Acetic acid was mixed in titanium butoxide. The molar ratio of titanium butoxide, acetic acid and n-butanol was 1:4:4. The atomic ratio of vanadium was calculated based on the desired V/Ti ratio and added in butanol. Then, the above two solution were mixed and hydrolyzed by the water generated via the esterification of acetic and butanol. The hydrolysis was completed after 24 h, then the solution was dried at 150 °C and pulverized to powder. The dried gel was then calcined at 400 °C for 30 min. The catalysts prepared by this procedure were assigned V/TiO_2-NE.

The second method was carried in a cooled acidic aqueous solution shown in Fig. 2. Vanadium chloride was dissolved completely in ethanol, then mixed into titanium butoxide. The volume of ethanol was 10 times of ethanol/titanium butoxide solution. The amount of vanadium was calculated based on the desired V/Ti ratio. The mixed solution was slowly drop-by-drop added in a 0.1 M HCl solution, which volume was 10 times of ethanol/titanium butoxide solution, and quickly hydrolyzed due to large amount of water. During this process, the solution was kept cooled at near 0 °C in a bath by circulating chilled water. The solution was dried at 110 °C, then following the same procedure of the first method. The catalysts prepared by this procedure were assigned V/TiO_2-C.

2.2. Characterization

The specific surface area of the V/TiO_2 catalyst was measured by N_2 adsorption using a Micrometrics ASAP 2010. A diffuse reflectance UV-Vis Spectrophotometer (HITACHI,
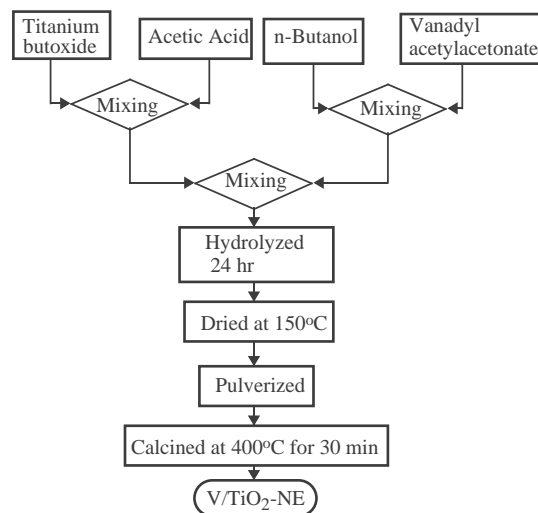

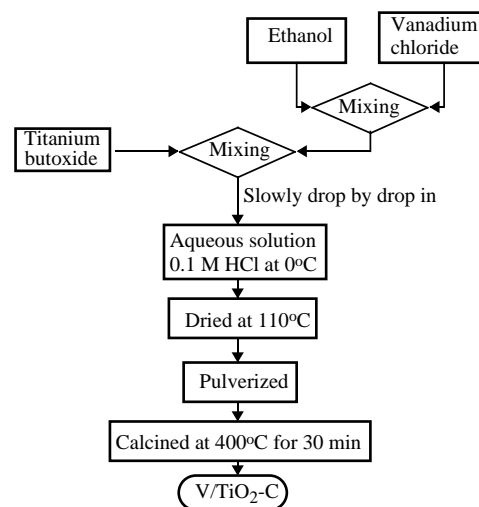Fig. 1. Procedure of catalysts by non aqueous sol–gel, V/TiO_2-NE.

Fig. 2. Procedure of catalyst by cooled water hydrolysis, V/TiO_2-C.

U3410) was employed to obtain the UV-Vis absorption spectra. The crystalline phase was identified by X-ray diffractometry (XRD) on a MAC (model M03XHF, Material Analysis and Characterization, Japan). X-ray photoelectron spectroscopy (XPS) was performed using VG Microtech MT500, operated with a constant pass energy of 50 eV and with Mg Kα radiation as the excitation source ($h\nu = 1253.6$ eV). The catalyst was pressed into a pellet, and then adhered on a sample holder by carbon tape. Oxygen (1s, 530.7 eV for TiO_2) and carbon (1s, 284.5 eV) were taken as internal standards for binding energy calibration. A transmission electron microscope (TEM), Hitachi H-7100, was applied to observe the morphology of catalysts and estimate the particle size.

The X-ray absorption spectra (XAS) of the V and Ti K-edge for the catalysts were measured at the Wiggler 17C station of the Taiwan Synchrotron Radiation Center in Hsinchu Science-based Industrial Park. Fluorescence mode was used to measure vanadium in titania catalysts. The powder sample was pressed in a sample holder positioned at 45° to the incident X-ray beam in a sample box. The fluorescent X-rays from the sample passed through a Ti-filter and reached the detector. The filter was used to avoid the interference from other atoms or incident X-rays. The measurement of titanium was in transition mode directly. The X-ray photon energy varied across and beyond the absorption edge of the measured atom. For vanadium, it was in the range from 200 eV below the vanadium absorption edge at 5465 to 800 eV above it. The intensities of both fluorescent (I_f) and incident (I_o) X-rays were measured to calculate the absorption coefficient (μ) for the atoms of interest using the equation, $\mu x = I_o/I_f$, where x is the thickness of the sample. Spectral analysis followed the standard steps of background correction and normalization before the near edge absorption structure was determined. Moreover, the spectra of pure V_2O_4 and V_2O_5 powder were measured as standard references.
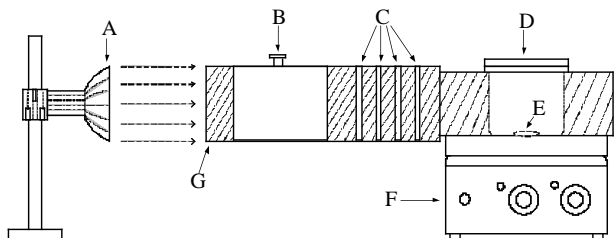
Fig. 3. Schematic of visible-light photo reaction system: (A) light; (B) IR filter (water); (C) UV filters; (D) Pyrex reactor; (E) magnetic rod; (F) stirrer; (G) light channel.

2.3. Photo degradation of crystal violet and methylene blue

The experiment of the CV or MB photo degradation was carried out in a visible-light Pyrex reactor. Fig. 3 depicts the visible-light photo reactor. The light source was a Philips CDM-R lamp with power 73 W and illumination 4850 lm. The IR (>700 nm) and UV (<400 nm) lights were filtered by a water bottle and UV filters, respectively. A background of MB or CV degradation was carried under irradiation without catalyst first. The photocatalytic degradation rate was calculated by subtracting the background rate.

A weight 0.05 g of catalyst powder was suspended in either crystal violet (CV) or methylene blue (MB) aqueous solution. The concentration of CV was 1.3×10^{-5} M prepared by dissolving 0.01 g in 350 ml de-ionized water. The amount of MB, 0.0037 g, was dissolved in 350 ml de-ionized water forming a 2.8×10^{-5} M solution. The solution was stirred and reached adsorption equilibrium with catalyst before a lamp was turned on to start the photo reaction. An UV-Vis spectrometer (Shimadzu, UV-210A) monitored the concentration changes of CV and MB using wavelength 590.5 and 661.0 nm, respectively. A linear calibration of absorption vs. concentration was obtained either CV or MB.

3. Results and discussion

3.1. Characteristics of catalysts

Table 1 summaries the specific surface area, mean pore size and pore volume of the catalysts and Degussa P25 titania. The V/TiO$_2$-C series gave specific surface area over 110 m^2/g, while those of V/TiO$_2$-NE ranged from 37 to 47 m^2/g. The pore sizes were in the meso pore region. Fig. 4(a) and (b) displays the TEM micrographs of V/TiO$_2$-C and V/TiO$_2$-NE, respectively, The particle sizes of V/TiO$_2$-C ranged from 6 to 8 nm, while those of V/TiO$_2$-NE were around 20 nm.

Fig. 5(A) and (B) show the XRD patterns of V/TiO$_2$-C and V/TiO$_2$-NE, respectively, indicating all anatase phases. All catalysts were stable in anatase using our preparation method, even after calcined temperature up to 700 °C. No characteristic peak of vanadium oxides (V$_2$O$_5$ and V$_2$O$_4$)
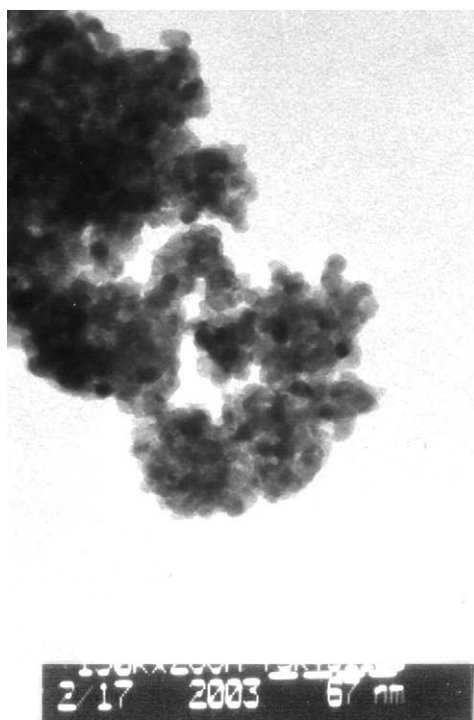
(a) 0.02 V/TiO2-C
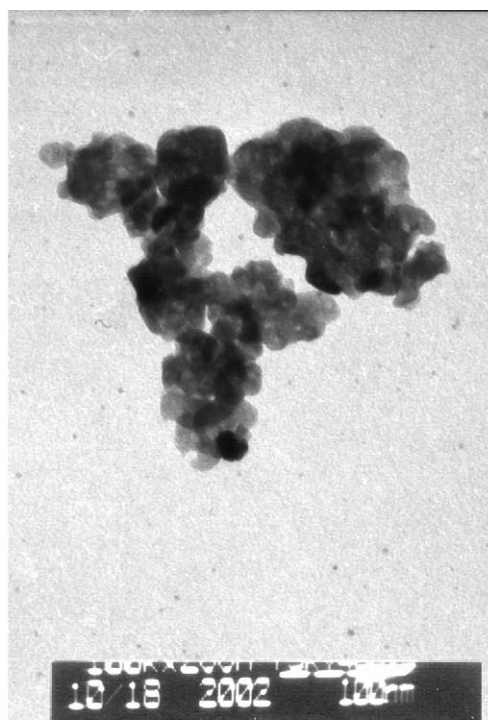
(b) 0.015 V/TiO2-NE

Fig. 4. Fig. 4(a) and (b) display the TEM micrographs: (a) 0.02-V/TiO$_2$-C; (b) 0.015-V/TiO$_2$-NE catalysts.

Table 1
Specific area, median pore size and pore volume of V/TiO$_2$ catalysts

| Catalyst	Specific area (m^2/g)	Median pore (nm)	Pore volume (cm^3/g)
0.01-V/TiO$_2$-C	112.6	4.4	0.16
0.02-V/TiO$_2$-C	116.8	4.4	0.17
0.029-V/TiO$_2$-C	117.5	4.4	0.16
0.035-V/TiO$_2$-C	128.6	4.5	0.16
0.052-V/TiO$_2$-C	127.6	4.6	0.16
0.025-V/TiO$_2$-NE	47.7	4.8	0.08
0.05-V/TiO$_2$-NE	41.6	6.4	0.09
0.08-V/TiO$_2$-NE	42.5	6.3	0.08
P25	53.7	12.3	0.17

Fig. 5. (A) XRD patterns of V/TiO$_2$-C catalysts calcined 400 °C: (a) V/Ti = 0.01, (b) V/Ti = 0.02, (c) V/Ti = 0.029, (d) V/Ti = 0.035, (e) V/Ti = 0.052; (B) XRD patterns of V/TiO$_2$-NE catalysts calcined at 400 °C: (a) V/Ti = 0.015, (b) V/Ti = 0.025, (c) V/Ti = 0.05, (d) V/Ti = 0.08.

were found in the XRD patterns implying either vanadium was incorporated in the crystalline of TiO$_2$, or vanadium oxide was very small and highly dispersed. The crystallite sizes estimated from peak broadening were consistent with the observation in TEM micrographs (Fig. 4). The crystallite size increased with increasing vanadium loading on both V/TiO$_2$ catalysts.

Fig. 6(A) and (B) show the UV-Vis absorption spectra of V/TiO$_2$-C and V/TiO$_2$-NE, respectively. The spectrum of pure TiO$_2$, which was prepared by our method, is shown in Fig. 6(B) and is similar to that of Degussa P25 in Fig. 6(A). Compared with the spectrum of pure titania, the red-shift was clearly observed in the series of V/TiO$_2$-C and V/TiO$_2$-NE catalysts. The higher the vanadium doping, the greater red-shift was. The UV-Vis spectrum of V$_2$O$_5$ also displays in Fig. 7(a) for comparison. The tailing of absorption curves reveal that V/TiO$_2$ absorb the photon energy in the range of 380–750 nm, and is different from that of pure V$_2$O$_5$ (near 500 nm). The band gaps of catalysts are in the range of 3.2∼2.8 eV. The 3d orbital of vanadium might change the band gap of titania so that V/TiO$_2$ catalysts enable to absorb visible light.

The chemical status of vanadium was evaluated by XPS as shown in Fig. 7. Both V/TiO$_2$-C and V/TiO$_2$-NE gave the similar spectra. The signal of characteristic peaks of vanadium was very weak. The magnitude was so small that was comparable with the oxygen satellite peak. The binding energy of vanadium was near 517.3 eV indicating V^{5+} species [9]. However, a shoulder of the peak at 516.1 eV suggested V^{4+} species, too. XPS can only measure the elements on the most outer surface. Only very few vanadium was on the surface of the TiO$_2$ particles indicating most vanadium located inside TiO$_2$.

Fig. 8(A) and (B) show the X-ray adsorption near edge structure (XANES) of vanadium in V/TiO$_2$-C and V/TiO$_2$-NE, respectively. The XANES of titanium in V/TiO$_2$ was found the same as that in pure anatase TiO$_2$, but significantly different from that in pure rutile TiO$_2$. Such result of anatase phase was consistent with the XRD pattern. The XANES of pure V$_2$O$_4$ and V$_2$O$_5$ were also measured and depicted in Fig. 8 for the comparison of either V^{4+} or V^{5+}. An absorption pre-edge at 5470 eV was observed in
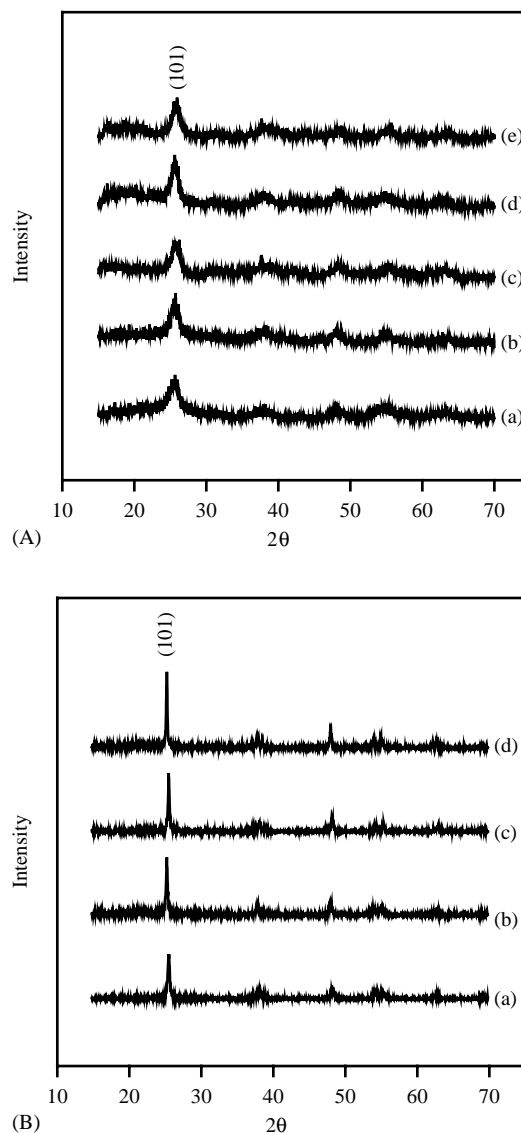
either V$_2$O$_4$ or V$_2$O$_5$. The shape of absorption pre-edge from V/TiO$_2$-C and V/TiO$_2$-NE is symmetric and closed to that of V$_2$O$_5$. Three post-edge absorption peaks, 5486, 5494 and 5506 eV can be found in V$_2$O$_5$. The post-edge absorption peaks of V$_2$O$_4$ are located near 5482, 5489 and 5502 eV, although they are not sharp. The XANES's of V/TiO$_2$-C and V/TiO$_2$-NE are all similar, and show two post-edge absorption peaks at 5488 and 5501 eV. Those two peaks may be composed of those peaks of V$_2$O$_5$ and V$_2$O$_4$. Therefore, the chemical status of vanadium in V/TiO$_2$-C and V/TiO$_2$-NE co-existed both V^{4+} and V^{5+}. The chemical status is an important evidence to deduce whether vanadium is located in the TiO$_2$ octahedral lattice. The V^{4+}

Fig. 7. XPS of vanadium $2p_{3/2}$ spectra of V/TiO$_2$-C: (a) V/Ti = 0.035, (b) V/Ti = 0.052.
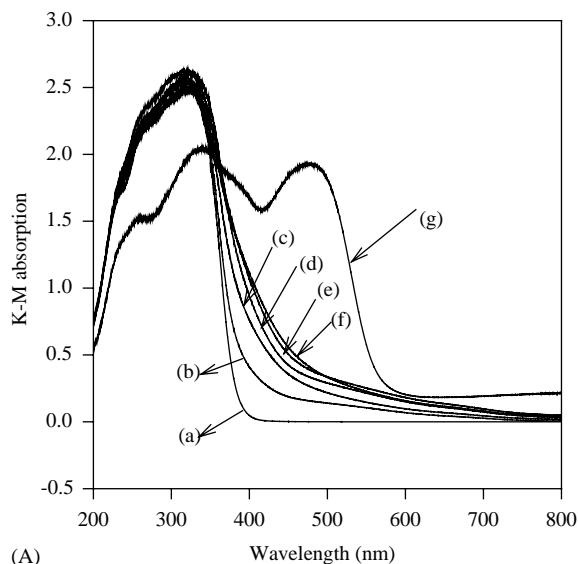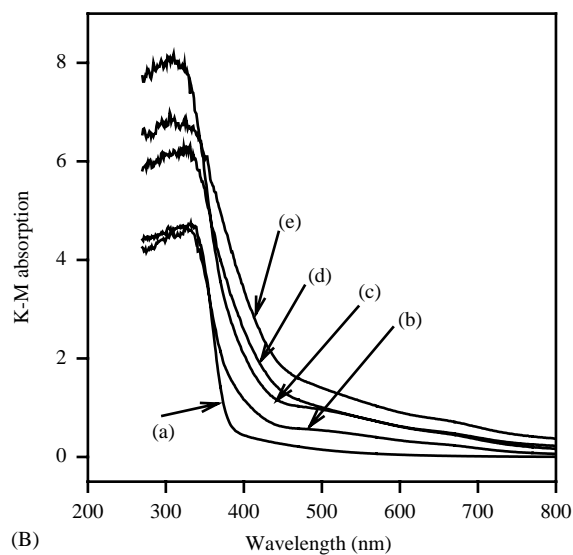
Fig. 6. (A) UV-Vis absorption spectra of V/TiO$_2$-C: (a) P25, (b) V/Ti = 0.01, (c) V/Ti = 0.02, (d) V/Ti = 0.029, (e) V/Ti = 0.035, (f) V/Ti = 0.052, (g) V$_2$O$_5$; (B) UV-Vis absorption spectra of V/TiO$_2$-NE: (a) TiO$_2$-NE, (b) V/Ti = 0.015, (c) V/Ti = 0.025, (d) V/Ti = 0.05, (e) V/Ti = 0.08.

V/TiO$_2$-NE irradiated under visible light at ambient temperature. The rate was calculated based on a 6-h irradiation, and was found zeroth order at the experimental conditions. The catalyst, 0.035 V/TiO$_2$-C, showed the highest rates 3.07×10^{-7} and 3.87×10^{-7} mol/l h of CV and MB, respectively. The maximum photo reaction rates of CV and MB were 3.61×10^{-7} and 3.71×10^{-7} mol/l h, respectively, on 0.05 V/TiO$_2$-NE. The pure TiO$_2$ was expected to be no photo activity but showed perceivable photo reaction rates because of a little portion of residue UV entering photo reactor. Table 3 lists the photon intensity of original light source and after IR and UV filters indicating a small port of UV-A and UV-C can enter the photo reactor. After UV portion was filtered, the photon intensity of UV-A and UV-C were reduced to only 1.0 and 10.6 μW/cm^2, respectively, compared with near 40,000 μW/cm^2 of visible light.

is possible in the octahedral lattice of TiO$_2$, while V^{5+} may be V$_2$O$_5$ highly dispersed within crystalline of TiO$_2$.

3.2. Photocatalytic activity

The photocatalytic activity of V/TiO$_2$ catalyst was tested by the de-colorization of CV and MB solutions. A CV molecule can be degraded into aryl compounds representing the photo oxidation activity [10]. A cationic form of MB can be reduced and changed blue to colorless by accepting an electron representing the photo reduction activity [11]. Table 2 lists the photo degradation rates of V/TiO$_2$-C and
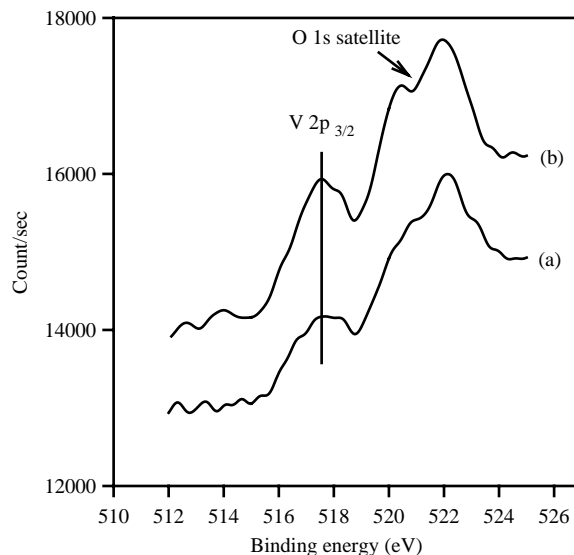
Table 2
Photo degradation rates of crystal violet (CV) and methyl blue (MB) with initial concentration, 1.3×10^{-5} and 2.8×10^{-5} M, respectively, under visible-light irradiation

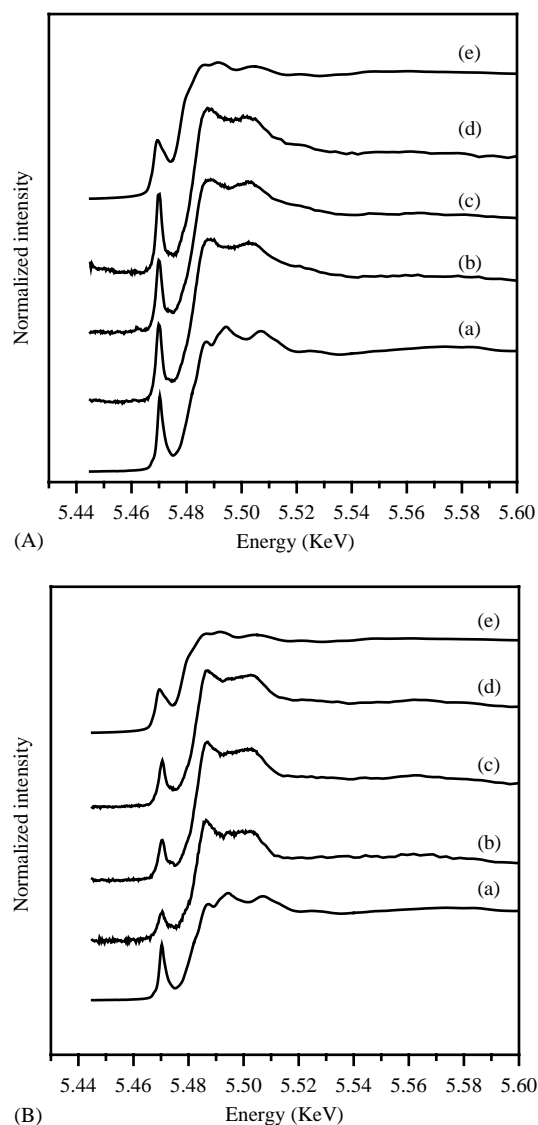| Catalyst	CV rate (10^{-7} mol/l h)	MB rate (10^{-7} mol/l h)
TiO$_2$-C	1.73	2.02
0.01-V/TiO$_2$-C	0.67	2.70
0.02-V/TiO$_2$-C	1.30	3.90
0.029-V/TiO$_2$-C	2.55	3.12
0.035-V/TiO$_2$-C	3.07	3.87
0.052-V/TiO$_2$-C	2.21	3.62
TiO2-NE	2.44	3.01
0.015-TiO$_2$-NE	2.44	3.17
0.025-TiO$_2$-NE	2.12	3.67
0.05-TiO$_2$-NE	3.61	3.71
0.08-TiO$_2$-NE	2.26	3.18

Fig. 8. (A) Vanadium XANES of V/TiO$_2$-C: (a) V$_2$O$_5$, (b) V/Ti = 0.029, (c) V/Ti = 0.035, (d) V/Ti = 0.052, (e) V$_2$O$_4$; (B) vanadium XANES of V/TiO$_2$-NE, (a) V$_2$O$_5$, (b) V/Ti = 0.025, (c) V/Ti = 0.05, (d) V/Ti = 0.08, (e) V$_2$O$_4$.

A photo reaction is initiated by the electron and hole via the excitation of photons. The transformation of photons to electron/hole pair, i.e., quantum efficiency, is one of crucial factors in a photo reaction. The quantum efficiency of UV light is much higher than that of visible light because of its

high photon energy. Therefore, even a small amount of UV can activate photo reaction effectively than that of visible light. In addition, both TiO$_2$ and V/TiO$_2$ catalyst have higher UV absorption efficiency than visible light. The absorption of visible light on V/TiO$_2$ is higher than that on pure TiO$_2$ as shown in Fig. 6. However, the enhancement of photo activity by visible-light is still surpassed by small amount of UV. not so drastically. That's why only marginally increasing photo activity were observed in V/TiO$_2$ catalysts under visible-light irradiation.

4. Conclusion

The modified sol–gel methods offer successful routes to synthesize V-doped titania catalysts. Vanadium ion in TiO$_2$ may change the band gap between conduction and valence bands. Thus, V-doped titania acquires the capability of absorbing visible light and shows a 'red-shift' in the UV-Vis spectra. The results of photocatalytic reaction indicate that the V-doped TiO$_2$ has higher activity than pure TiO$_2$ under visible light irradiation. The improvement is due to the highly dispersed vanadium in the TiO$_2$ crystallite.

Table 3
The filtering results of UV light

	UV-A (μW/cm^2)[a] 365 nm	UV-C (μW/cm^2)[a] 254 nm
Original light	1023.5	18.1
IR and UV filtered	1.0	10.6

[a] Measured by a Lumen meter with specific wavelength at 365 or 254 nm.

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