Preparation and characterization of ZnO/TiO$_2$ for the photocatalytic reduction of Cr(VI) in aqueous solution

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ABSTRACT

ZnO/TiO$_2$ photocatalysts coupled with various ZnO dosages (0.5–10 mol%) were prepared by wetness impregnation method and characterized in this study. X-ray photoelectron spectroscopy results indicated that zinc ions did not enter TiO$_2$ lattice and was more likely to bond with oxygen atoms to form ZnO coupled on the surface of TiO$_2$. The coupling of ZnO on the surface of TiO$_2$ retarded the crystal phase transformation from anatase to rutile phase for TiO$_2$ calcined at temperatures higher than 500 °C. The specific surface area of ZnO/TiO$_2$ calcined at 700 °C was notably higher than that of pure TiO$_2$ possibly because the aggregation and agglomeration of particles were inhibited by the indirect contact of TiO$_2$ particles during the calcination. Photocatalytic reduction of hexavalent chromium, Cr(VI), in aqueous solutions using ZnO/TiO$_2$ was evaluated under 365 nm UV light illumination. ZnO/TiO$_2$ containing 2.0 mol% ZnO exhibited the lowest photoluminescence emission intensity and the maximum photocatalytic reduction of Cr(VI) in aqueous solutions due to the enhancement of charge separation by interparticle electron transfer. However, excessive ZnO on the surface of TiO$_2$ may serve as recombination centers of electron–hole pairs to decrease the photocatalytic activity of ZnO/TiO$_2$. Moreover, the decreased photocatalytic reduction of Cr(VI) using ZnO/TiO$_2$ calcined at higher temperatures was assumed to be attributed to the decrease of specific surface areas.

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1. Introduction

Increasing concerns on various environmental contaminations has stimulated vital development of various treatment technologies. Photocatalytic processes using semi-conductors as catalysts under appropriate illumination are attracting extensive attention mainly because of the relatively mild reaction conditions required to the satisfactory decomposition of refractory pollutants. Numerous innovative technologies associated with TiO$_2$-assisted photocatalytic reactions were developed intensively for the decomposition of numerous organic compounds in aqueous and gaseous streams [1,2]. Recently, the application of photocatalytic reduction process using TiO$_2$ is reported to effectively reduce various heavy metals in aqueous solutions to less-toxic states. Ku and Jung [3] investigated the hexavalent chromium, Cr(VI), reduction in aqueous solution by the photocatalytic process and indicated that Cr(VI) was reduced almost completely within 5 h for experiments conducted in acidic solutions containing 0.5% ethanol. Yoon et al. [4] also revealed that the photocatalytic reduction of Cr(VI) was favored in acidic solutions because of the electrostatic affinity between Cr$_2$O$_7^{2-}$ and TiO$_2$. Jiang et al. [5] demonstrated that

the prepared sulfated TiO$_2$ photocatalyst provided an acid environment over the catalyst surface to markedly promote the reduction of Cr(VI).

Titanium dioxide (TiO$_2$) is the most studied photocatalyst for environmental applications because it is photocatalytically stable, inexpensive, and harmless. However, electron transfer and the recombination between electron–hole pairs results in low quantum yields for most photocatalytic reactions [6]. The application of coupled semiconductors in the photocatalytic process is regarded as an alternative to enhance the photocatalytic activity of photocatalyst by inhibiting the recombination of electron–hole pairs [7]. ZnO is considered to be a suitable semiconductor to be coupled with TiO$_2$ due to its high photocatalytic activity, approximative band gap energy and similar photocatalytic mechanism of reaction as compared to TiO$_2$ [8,9]. Serpone et al. [10] indicated that the transfer of electrons and holes using ZnO/TiO$_2$ semiconductors is important in the photocatalytic oxidation of aromatic compounds and proposed the transfer mechanism of electrons and holes at the interface of the coupled photocatalyst as shown in Fig. 1. ZnO and TiO$_2$ possessed different redox energy levels for their corresponding conduction and valance bands. Once illuminated UV light induced electron–hole pairs on ZnO and TiO$_2$ surfaces simultaneously, the difference of redox energy levels between the two semiconductors drove the charge separation to enhance the photocatalytic activity.

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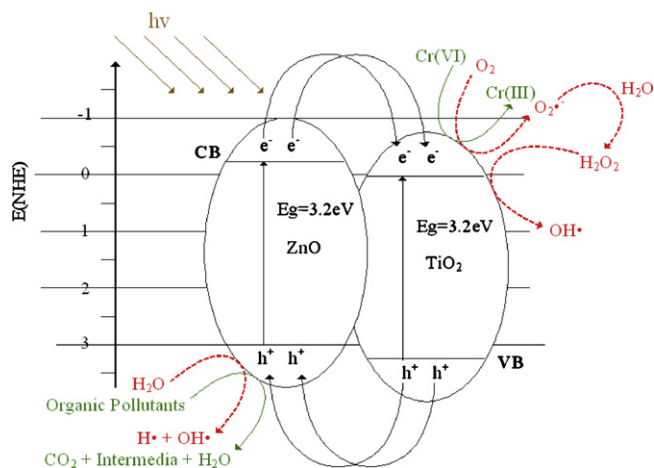*E-mail address:* ku508@mail.ntust.edu.tw (Y. Ku).

Fig. 1. Schematic diagram of transfer mechanism of electrons and holes for photo-catalytic process using ZnO/TiO₂.

Shifu et al. [11] prepared ZnO/TiO₂ by ball milling of TiO₂ and ZnO particles in H₂O solution. The authors indicated that no intense peak of ZnO was observed for ZnO/TiO₂ containing ZnO lower than 5 wt% because ZnO particles were highly dispersed on the TiO₂ surface or between the interfaces of TiO₂ aggregates. Zou et al. [12] fabricated ZnO/TiO₂ nanoparticles by sol–gel method and demonstrated that Zn was distributed on the surface of TiO₂ in the form of ZnO. Their experimental results also indicated that the coupling of ZnO on the TiO₂ surface retarded the aggregation of particles because ZnO particles distributed on the surface of TiO₂ might avoid the direct contact of TiO₂ particles during calcination. Wang et al. [13] investigated effect of ZnO coupling dosage of ZnO/TiO₂ on the photocatalytic oxidation of nitric oxide. The authors indicated that the photocatalytic activity of ZnO/TiO₂ was higher than the Degussa P-25 TiO₂, and ZnO/TiO₂ containing 0.5% ZnO demonstrated highest photocatalytic activity.

The objective of this study is to fabricate ZnO/TiO₂ coupled photocatalysts with various ZnO dosages by wetness impregnation method. ZnO/TiO₂ coupled photocatalysts were characterized using a series of materials analysis techniques, such as Brunauer–Emmett–Teller surface area measurements, X-ray diffraction, X-ray photoelectron spectroscopy, and photoluminescence emission spectra. Effect of the coupled ZnO dosage on the photocatalytic reduction of hexavalent chromium in aqueous solution was also studied. The reaction rates were determined under various operating conditions and the rate parameters were expressed in terms of an apparent first order rate equation.

2. Materials and methods

ZnO/TiO₂ coupled photocatalyst was prepared by wetness impregnation method in this study. Predetermined amount of reagent grade ZnSO₄·7H₂O was added into 40 ml double deionized water, and the solution was vigorously stirred by a magnetic stirrer until zinc sulphate dissolved completely. Certain amount of Degussa P-25 TiO₂ powder was suspended in this solution, and the suspension was subsequently sonicated for 1 h at room temperature. Then the suspension was aged at room temperature for 8 h and was sonicated again for 12 h. Finally, the suspension was dried isothermally at 80 °C for 12 h, and then the residual was put into the muffle furnace at various temperatures for 3 h for calcination. The phase and lattice parameters of prepared photocatalyst were determined by a D/MAX-RC X-ray diffractometer equipped with Cu Kα at 40 kV. The BET specific surface area of the prepared photocatalyst was measured by N₂ adsorption at 250 °C using an adsorption
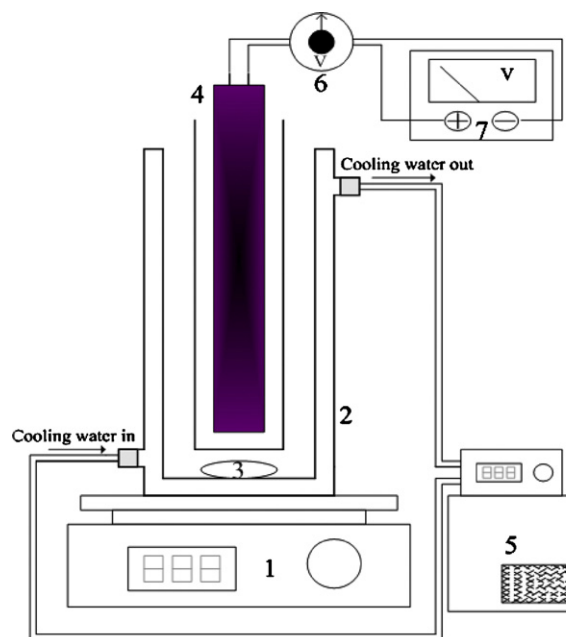
1. Magnetic Stirrer, 2. Pyrex Photoreactor, 3. Magnet, 4. UV Lamp, 5. Isothermal Controller, 6. Variable Voltage Transformer, 7. Power Supply.

Fig. 2. Schematic diagram of the photocatalytic system. 1 – Magnetic stirrer, 2 – Pyrex photometer, 3 – magnet, 4 – UV lamp, 5 – isothermal controller, 6 – variable voltage transformer, 7 – power supply.

instrument (Quantachrome, Autosorb-1). Chemical bindings and composition of the coupled photocatalyst were investigated by the X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD). Photoluminescence (PL) emission spectra of the prepared samples were recorded at room temperature with a spectrometer (Horiba Jobin Yvon iHR 550) equipped with a He–Cd laser lamp at an excitation wavelength of 325 nm.

The schematic diagram of the photocatalytic reaction system is shown in Fig. 2. Aqueous solution containing 20 mg/l Cr(VI) and 0.2 g photocatalyst was put into the inter-irradiation-type Pyrex photoreactor with effective volume of 200 ml. The batch photoreactor was water-jacketed to maintain the solution temperature at 25 °C during experiments. A 10 W low-pressure mercury lamp with emitted wavelength mainly of 365 nm was used as light source in this study. The solution pH was controlled at 5.5 by dripping the 1 N HNO₃ and NaOH solutions. The prepared suspension was stirred without irradiation for 30 min to achieve adsorption equilibrium. Photocatalytic reduction of Cr(VI) was assumed to be started when the pre-warmed light source within the reactor was turned on. Aliquots of reaction solution were then sampled at each intermittent periods, and were measured for Cr(VI) concentration of by an UV–visible spectrophotometer (Jasco, V-550) at the wavelength of 349 nm.

3. Results and discussion

3.1. Characterization of ZnO/TiO₂

In this study, ZnO/TiO₂ photocatalysts containing various coupled ZnO dosages (0.5, 2.0, 4.0 and 10.0 mol%) were prepared by wetness impregnation method and calcined at temperatures ranging from 300 to 700 °C. The XRD patterns of the ZnO/TiO₂ photocatalysts containing various coupled ZnO dosages at an angle of 2θ from 20 to 80° are presented in Fig. 3. It is noticed that the diffraction peak intensities of both anatase and rutile were decreased
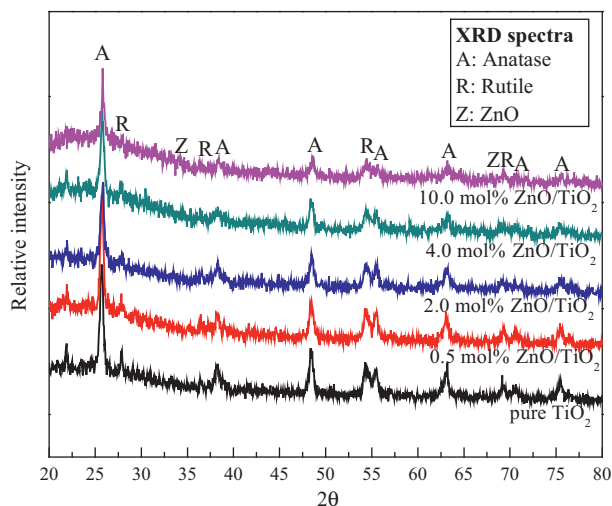
Fig. 3. XRD patterns of pure TiO_2 and ZnO/TiO_2 coupled with various ZnO dosages.

Table 1
Effects of calcined temperature on the specific surface area for pure TiO_2 and ZnO/TiO_2 with various coupled dosage of ZnO.

Coupled ZnO dosage (mol%)	Specific surface area (m²/g)				
	300 °C	400 °C	500 °C	600 °C	700 °C
Pure TiO_2	53	50	48	46	10
0.5	54	53	50	47	21
2	53	49	47	42	21
4	49	48	40	38	22
10	49	47	40	34	24

with the increase of coupled ZnO dosage, possibly because the highly dispersed ZnO particles might shelter the TiO_2 surface from the emitted X-ray diffraction. Moreover, no intense peak of zinc oxide was observed for samples examined in this study because the amount of coupled ZnO might be too low to be detected, similar to the experimental results reported by Shifu et al. [11] and Zou et al. [12].

Fig. 4 shows the XRD patterns of 2.0 mol% ZnO/TiO_2 calcined at temperatures ranging from 300 to 700 °C. Both anatase and rutile phases of TiO_2 could be observed from the XRD spectra of 2.0 mol% ZnO/TiO_2. The phase transformation from anatase to rutile was found to be enhanced for samples calcined at higher temperatures. Almost no intense peak of anatase phase ($2\theta = 25.306°$) for pure TiO_2 could be observed at the calcined temperature of 700 °C for most photocatalytic researches. The crystal phase transformation was found to be less evident for ZnO/TiO_2 calcined at temperatures higher than 500 °C as compared to pure TiO_2. Zou et al. [12] also reported this phenomenon and indicated that the presence of ZnO on the surface of TiO_2 might inhibit the phase transformation.

Effects of calcined temperature on the specific surface areas for pure TiO_2 and ZnO/TiO_2 with various coupled dosages of ZnO are listed in Table 1. The specific surface areas of pure TiO_2 and ZnO/TiO_2 with various coupled ZnO dosages slightly decreased
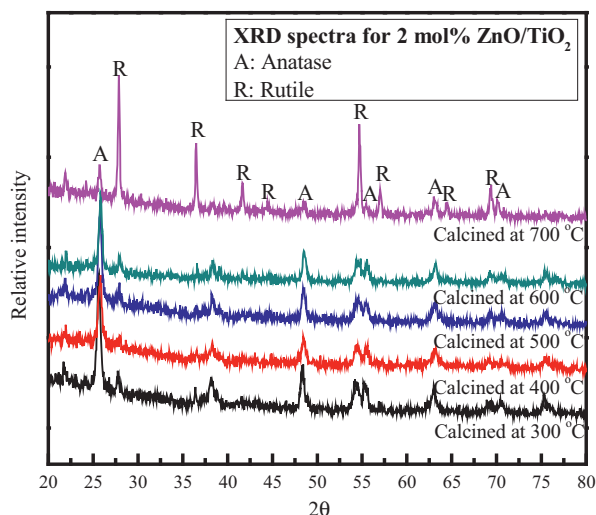
with increasing calcined temperature from 300 to 600 °C and then severe decreased for those calcined at 700 °C, possibly because the particles of photocatalyst were aggregated. It was also found that the specific surface area of ZnO/TiO_2 calcined at 700 °C was significantly higher than that of pure TiO_2. Zou et al. [12] indicated that the coupling of ZnO on the TiO_2 surface might avoid the direct contact of TiO_2 particles during the calcination and thereby retarded the aggregation and agglomeration of ZnO/TiO_2 particles.

The high resolution XPS spectra of the Ti2p and Zn2p regions for TiO_2 and ZnO/TiO_2 are shown in Fig. 5. As illustrated in Fig. 5(a), the binding energies of Ti2p region exhibited two peaks at 458.8 eV and 464.3 eV corresponding to $Ti2p_{3/2}$ and $Ti2p_{1/2}$, respectively, designated to the presence of Ti^{4+}. Spectrum of Zn2p region depicted in Fig. 5(b) demonstrated two peaks at 1021.8 eV ($Zn2p_{3/2}$) and
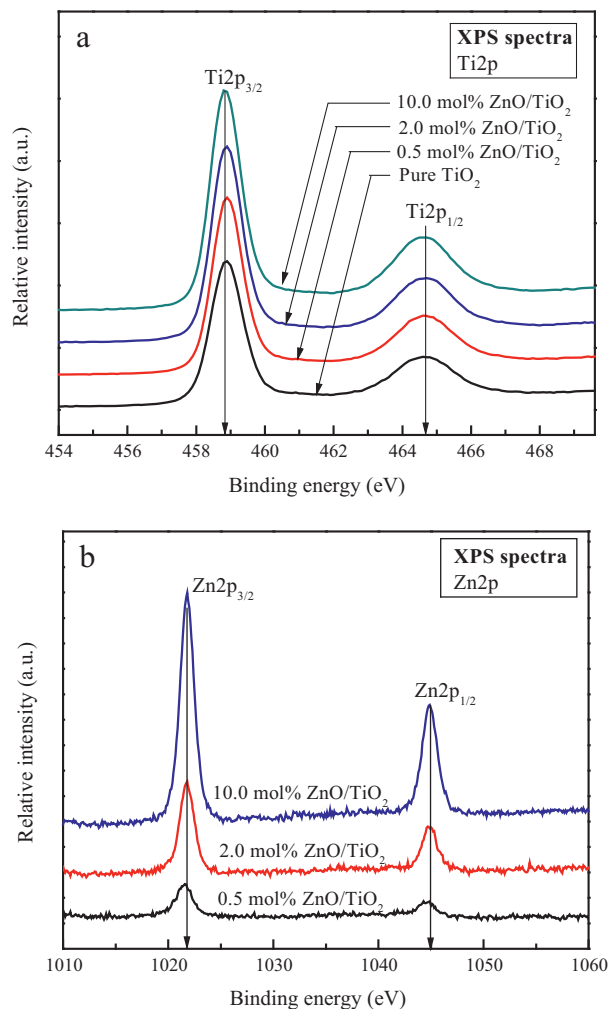

Fig. 4. XRD patterns of 2 mol% ZnO/TiO_2 under various calcination temperatures.

Fig. 5. High resolution XPS spectra of (a) Ti2p region and (b) Zn2p region for pure TiO_2 and ZnO/TiO_2 coupled with various ZnO dosages.
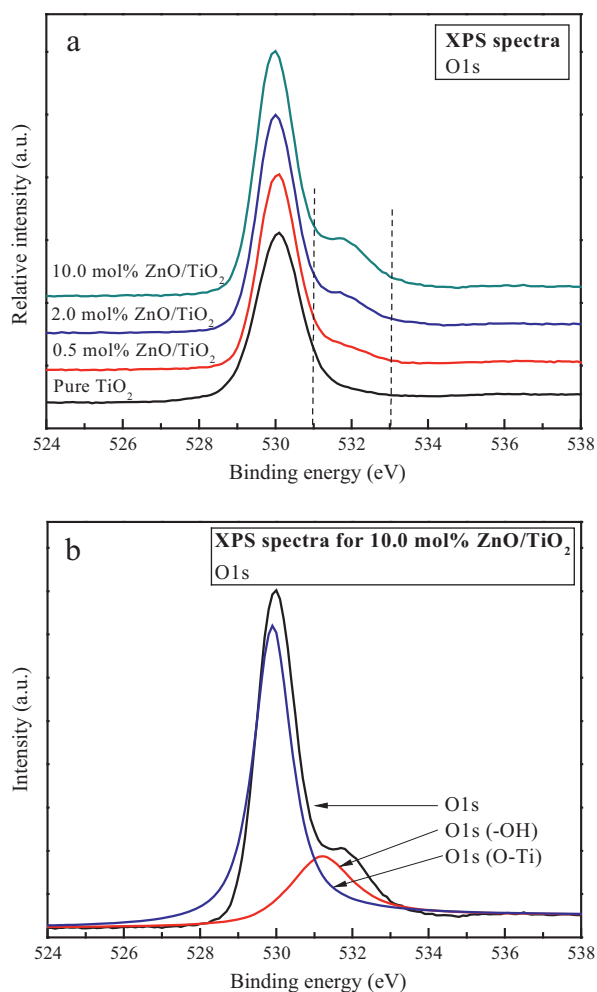
Fig. 6. High resolution XPS spectra of the O1s region for (a) pure TiO₂ and ZnO/TiO₂ coupled with various ZnO dosages and (b) ZnO/TiO₂ coupled with 10 mol% ZnO.

Table 2
Contributions of O–Ti and –OH bonding to the O1s oxygen atoms for pure TiO₂ and prepared ZnO/TiO₂ coupled with various ZnO dosages.

Coupled ZnO dosages	γ_i[a](%)	
	O1s (O–Ti, 529.9 eV)	O1s (–OH, 531.2 eV)
Pure TiO₂	~100.00	~0.00
0.5 mol%	85.12	14.88
2.0 mol%	79.83	20.17
10.0 mol%	74.10	25.90

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

abundant hydroxyl groups resulted from the coupling of metal oxides were more capable to accept the light-induced holes and to oxidize organic molecules adsorbed on TiO₂ surface.

ZnO/TiO₂ may absorb the photons with enough energy to generate electron–hole pairs, and the subsequent recombination of the photoexcited electrons and holes can release energy in the form of photoluminance (PL). Therefore, several previous researchers [17–19] reported that lower PL emission intensities might indicate lower recombination of electron–hole pairs. In this study, the PL emission spectra of pure TiO₂ and prepared ZnO/TiO₂ using a He–Cd laser light with 325 nm wavelength are depicted in Fig. 7. The PL emission intensities of pure TiO₂ and prepared ZnO/TiO₂ exhibited peak values at approximately 405 nm corresponding 3.07 eV. Pure TiO₂ sample demonstrated the highest PL emission intensity, indicating that electrons and holes were more easily recombined. The PL emission intensity was found to be decreased with the coupling of ZnO, possibly because the different redox energy levels of conduction and valance bands for ZnO and TiO₂ led to the interfacial charge transfer to inhibit the recombination of electron–hole pairs. The PL emission spectrum for ZnO/TiO₂ containing 2.0 mol% ZnO was much lower than those for pure TiO₂ and ZnO/TiO₂ containing 10.0 mol% ZnO. The recombination was recommenced for ZnO/TiO₂ containing excessive dosages of ZnO because the new recombination centers provided by the abundant ZnO particles [13].

3.2. Photocatalytic activity of ZnO/TiO₂

Experimental results of photocatalytic reduction of Cr(VI) in aqueous solutions were carried out by using pure TiO₂ and prepared ZnO/TiO₂ under 365 nm UV irradiation. The calculated apparent first-order rate constants are shown in Fig. 8. Experiments conducted with ZnO/TiO₂ demonstrated much higher Cr(VI) reduction rates than that conducted with pure TiO₂, amongst ZnO/TiO₂ con-
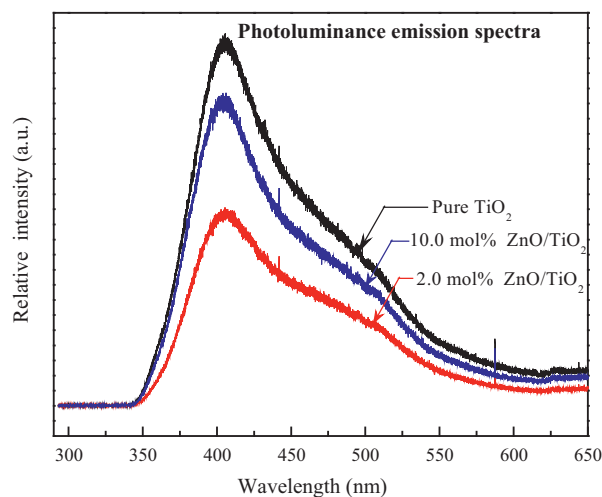
1044.7 eV (Zn2p$_{1/2}$), indicating that Zn²⁺ was bonded with oxygen atoms to form ZnO. These results provided the evidence that zinc ions did not enter TiO₂ lattice, but existed as ZnO particles, because there was no other Zn2p peak appeared in XPS spectra.

The high resolution XPS spectra of O1s on the surface of pure TiO₂ and prepared ZnO/TiO₂ are shown in Fig. 6. As shown in Fig. 6(a), the broad and asymmetric peak of O1s was partitioned into two peaks, 529.9 eV and 531.2 eV, corresponding to O–Ti bonding of TiO₂ and hydroxyl group (–OH) on the surface of ZnO/TiO₂, respectively, referring to the results reported by Yu et al. [14]. The results of curve fitting of high resolution XPS spectra for the O1s region of ZnO/TiO₂ containing 10.0 mol% ZnO are displayed in Fig. 6(b). As the results shown in Fig. 6, the full width at half maximum (FWHM) of O1s peak at 529.9 eV for ZnO/TiO₂ was found to be slightly increased due to the overlapping of the O–Zn and O–Ti bindings. This phenomenon also implied that the coupled Zn ions existed as ZnO on TiO₂ surface. Moreover, the surface-bound hydroxyl groups were considered to be the chemically adsorbed H₂O, because physically adsorbed H₂O should be easily desorbed in the super high vacuum surrounding of XPS system. The contributions of O–Ti and –OH bonding to the oxygen atoms for pure TiO₂ and prepared ZnO/TiO₂ are calculated and listed in Table 2. The contribution of hydroxyl group was found to increase significantly with increasing ZnO dosage. Papp et al. [15] and Fu et al. [16] prepared the TiO₂/WO₃, TiO₂/MO₃, TiO₂/SiO₂, and TiO₂/ZrO₂ photocatalysts and indicated that the TiO₂ surfaces covered with

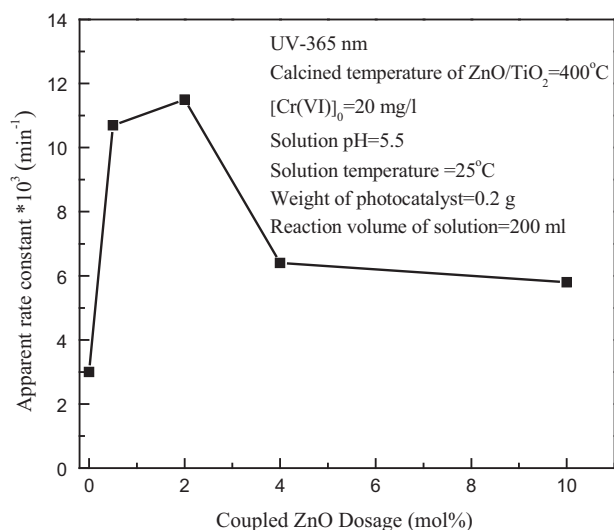**Fig. 7.** Photoluminance spectra of pure TiO₂ and ZnO/TiO₂ coupled with various ZnO dosages.

Fig. 8. Effect of coupled ZnO dosage on the apparent reaction rate constant for photocatalytic reduction of Cr(VI) in aqueous solutions.

taining 2.0 mol% ZnO exhibited highest reduction rate. Based on the transfer mechanism of electrons and holes at the interface of ZnO/TiO$_2$ reported by previous researchers as presented in the Introduction section, the enhanced photocatalytic activity for Cr(VI) reduction is possibly because that the difference of redox energy levels between ZnO and TiO$_2$ drove the charge separation to inhibit the recombination of electron–hole pairs. The reduction of Cr(VI) tended to be retarded for experiments conducted with ZnO/TiO$_2$ containing higher than 2.0 mol% ZnO. Shifu et al. [11] investigated the application of ZnO/TiO$_2$ on the photocatalytic oxidation of methyl orange, and also reported that ZnO/TiO$_2$ containing 2.0 mol% ZnO showed the highest photocatalytic activity. The authors attributed this phenomenon to the formation of new recombination centers of electron–hole pairs at the excessive dosages of ZnO. In addition, experimental results on the photocatalytic reduction of Cr(VI) conducted with ZnO/TiO$_2$ containing various dosages of ZnO were found to be agreed with the results on PL spectra previously shown in Fig. 7.

Fig. 9 shows the effect of calcined temperature of ZnO/TiO$_2$ containing 2.0 mol% ZnO on the calculated first-order photocatalytic
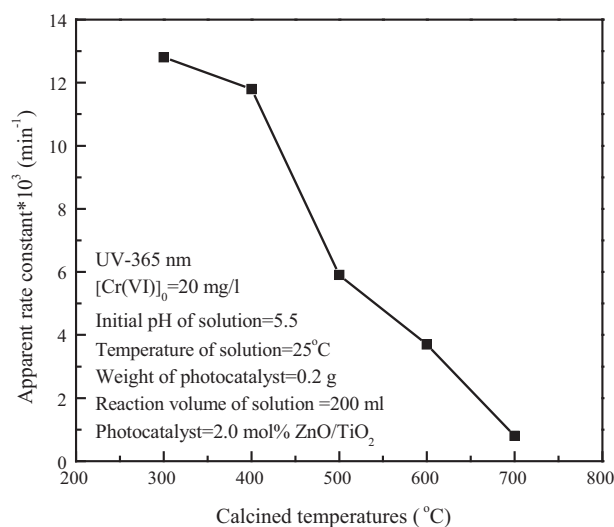

Fig. 9. Effect of calcined temperature on the apparent reaction rate constant for photocatalytic reduction of Cr(VI) in aqueous solutions.

reduction rate constant of Cr(VI). The reduction rate of Cr(VI) was decelerated using ZnO/TiO$_2$ calcined at higher temperatures. Liao et al. [20] also reported that the photocatalytic activity of ZnO/TiO$_2$ for methyl orange degradation decreased with increasing calcined temperature. The authors ascribed these results to the transformation of TiO$_2$ from anatase to rutile and to the appearance of ZnTiO$_3$. However, the phase transformation of TiO$_2$ from anatase to rutile at higher calcined temperatures was found to be inhibited by coupling of ZnO as shown in Fig. 4. No intense peak of the impurity of ZnTiO$_3$ was detected for samples examined in this study. As the BET results shown in Table 1, the specific surface area of ZnO/TiO$_2$ was decreased with the increase of calcined temperature because of the particle aggregation. Consequently, the decreased photocatalytic reduction of Cr(VI) was assumed to be attributed to the decrease of specific surface areas of ZnO/TiO$_2$ calcined at higher temperatures.

4. Conclusions

ZnO/TiO$_2$ photocatalysts containing various ZnO dosages prepared by wetness impregnation method and calcined at various temperatures were characterized in this study. Even through no intense XRD peak of zinc oxides was observed for samples examined, XPS results represented that zinc ions did not enter TiO$_2$ lattice and was more likely to bond with oxygen atoms to form ZnO on the surface of TiO$_2$. The coupling of ZnO on the surface of TiO$_2$ inhibited the crystal phase transformation from anatase to rutile phase for TiO$_2$ calcined at higher temperatures. ZnO/TiO$_2$ containing 2.0 mol% ZnO exhibited the lowest PL emission intensity and maximum photocatalytic reduction of Cr(VI) in aqueous solutions due to the enhancement of charge separation by interparticle electron transfer. However, the presence of excessive coupled ZnO may serve as new electron–hole recombination centers to reduce photocatalytic reduction of Cr(VI). The decrease of photocatalytic reduction of Cr(VI) using ZnO/TiO$_2$ calcined at higher temperatures was attributed to the decrease of specific surface areas of ZnO/TiO$_2$ induced by the aggregation and agglomeration of particles.

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