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Multichannel charge separation promoted ZnO/P25 heterojunctions for the photocatalytic oxidation of toluene

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ABSTRACT

The fabrication of multicomponent heterojunctions is an effective strategy to improve the performance of TiO₂ based photocatalysts. We provide a new strategy for improving the charge separation and photocatalytic performance of ZnO/TiO₂ composites by the formation of multichannel charge separated heterojunctions. ZnO/P25 composites were prepared by an incipient wetness impregnation method, and applied for the photocatalytic destruction of gaseous toluene. The ZnO/P25 composites consist of anatase TiO₂ (ATiO₂), rutile TiO₂ (RTiO₂) and hexagonal zincite structures. The parasitic phase of ZnO in P25 leads to the formation of ZnO(002)/ATiO₂(101)/RTiO₂(110) heterojunctions that exhibit enhanced light absorption and improved multichannel electron/hole separation. ZnO/P25 heterojunctions can completely oxidize toluene into CO₂ and H₂O under ultraviolet light irradiation at room temperature, and show enhanced photocatalytic activity in comparison with P25 owing to the efficient electron-hole separation. Such a multichannel charge separated design strategy may provide new insight into the design of highly effective photocatalysts and their potential technological applications.

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1. Introduction

Toluene is one of the most common toxic volatile organic compounds in an indoor environment, which is emitted from decoration materials, paint and cementing compounds, and poses a potential health risk to human beings even at a very low concentration level [1]. Recently, many methods have been proposed to remove trace toluene from air, such as adsorption [2], catalytic oxidation [3–5] and photocatalysis [6,7]. Among them, photocatalytic oxidation is one of the most effective and

economically feasible technologies because toluene can be photodegraded into CO₂ over photocatalysts under mild conditions.

TiO₂ has been one of the most widely studied photocatalysts for environmental applications, such as air purification and water purification, owing to its practicality and superior oxidation capability [8,9]. TiO₂ is usually used as a photocatalyst in two crystal structures: anatase TiO₂ (ATiO₂) and rutile TiO₂ (RTiO₂). However, both of them suffer from a low quantum yield in their technical application owing to the rapid recombina-

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nation of photo-induced electron-hole pairs [10]. Recently, various modifications have been performed that have focused on overcoming this barrier, including noble metal decoration [11,12] and the fabrication of multicomponent heterojunctions [13,14]. Various heterostructures have been reported to suppress the recombination of carriers, such as $\text{TiO}_2/\text{graphene}$ [15], CdS/TiO_2 [16], $\text{TiO}_2/\text{SnO}_2$ [17], $\text{Ag}_2\text{CO}_3/\text{TiO}_2$ [18] and ZnO/TiO_2 [19–25]. Among them, the combination of wurtzite ZnO with ATiO_2 has received particular attention because of the enhanced photocatalytic performance of ZnO/ATiO_2 and the low cost, non-toxic and high photocatalytic properties of ZnO [19]. The enhancement is ascribed to the formation of heterojunctions in the interface between ZnO and ATiO_2 and its function on the photo-induced electron-hole separation. Although the binding energies of ZnO and TiO_2 are analogous to each other, the potentials of the conduction band (CB) and the valence band (VB) of ZnO are still a little more negative than those of TiO_2 [20]. The electron transfer from the CB of ZnO to the CB of TiO_2 and the hole transfer from the VB of TiO_2 to the VB of ZnO proceed under illumination. As a result, the increase in the availability of the charges on the photocatalyst surface and consequently an improvement of the photocatalytic process can be expected. Kim et al. [21] reported that the photocurrent and the resulting photocatalytic properties of phenol decreased as the thickness of the ZnO layer increased in ZnO/TiO_2 nanoporous films, which was understood in terms of the function of ZnO/TiO_2 heterojunctions on the charge carrier lifetime. Moreover, as ZnO serves as excellent channels outstretched directly from ATiO_2 for the holes, the photocorrosion of ZnO is inhibited efficiently and the photostability of the ZnO/ATiO_2 hierarchical hybrid nanostructures can be enhanced [22].

To promote the charge separation and the photocatalytic performance of ZnO/ATiO_2 , various ZnO/ATiO_2 hybrid nanostructures with hierarchical morphology have been designed [19–25]. Chen et al. [23] prepared ZnO/ATiO_2 nanocomposites using a hydrothermal method. Xiao [24] fabricated three-dimensional arrayed ZnO/ATiO_2 nanotube heterostructure by a two-step anodization combined with a pyrolysis approach. Wu et al. [25] fabricated ZnO -nanorod framed ZnO/ATiO_2 heterostructures through a face-selective growth process, in which uniform ZnO nanorod arrays covered all eight $\{101\}$ faces, while the two highly reactive $\{001\}$ faces remained untouched. It was demonstrated that the photocatalytic performance of these coupled ZnO/ATiO_2 hierarchical hybrid nanostructures was enhanced to some extent owing to their unique heterostructures. However, owing to the synthetic complexity of the hybrid nanostructures and limited improvement in the charge separation by the morphology modification, the design of effective heterostructures for photocatalytic application, such as ZnO/TiO_2 , continues to be a challenge.

Herein, we provide a new strategy for improving the charge separation and photocatalytic performance of ZnO/TiO_2 by the formation of multichannel charge separation promoted heterojunctions. $\text{ZnO}/\text{TiO}_2(\text{P25})$ composites with different ZnO contents and calcination temperatures were synthesized by a facile incipient wetness impregnation method and applied for

the photocatalytic destruction of gaseous toluene. P25, consisting of anatase and rutile (4/1, w/w), has frequently been used as a benchmark for photocatalysts [10,26]. The parasitic phase of ZnO in P25 leads to the formation of $\text{ZnO}(002)/\text{anatase}(101)/\text{rutile}(110)$ junctions and enhances the light absorption. Especially, the multichannels for electron/hole separation in the as-formed heterojunctions remarkably improve the charge separation and photocatalytic performance of $\text{ZnO}/\text{P25}$ in comparison with P25.

2. Experimental

2.1. Catalyst preparation

$\text{ZnO}/\text{TiO}_2(\text{P25})$ composites were synthesized through the incipient wetness impregnation method. In a typical preparation experiment, P25 (Degussa) was uniformly dispersed into the aqueous solution containing the requisite amount of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., China) to obtain a ZnO loading amount of 0.1, 0.5 or 1 wt%. The samples were then dried at 120 °C overnight to evaporate the solvent and finally calcined at 300, 500, or 700 °C for 6 h with a heating rate of 10 °C/min in air, respectively. For comparison, ZnO powder was obtained by calcining $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ at 500 °C for 6 h with a heating rate of 10 °C/min in air. Some P25 powder was also calcined at 500 °C for 6 h with a heating rate of 10 °C/min in air for reference (P25-500). The as-prepared catalysts were respectively denoted as $\text{ZnO}/\text{P25}$ with the ZnO loading amount number in front and the calcination temperature behind for simplicity.

2.2. Catalyst characterization

The phase purity and crystal structure of the samples were examined by X-ray diffraction (XRD) using a D-MAX diffractometer with $\text{Cu K}\alpha$ radiation at a scanning rate of 10°/min and a step size of 0.02°. The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore size distribution of the samples were measured with a Micromeritics ASAP 2020 instrument using N_2 adsorption-desorption at -196 °C. Prior to the measurement, the samples were degassed at 300 °C for 3 h. The morphologies and compositions of the samples were analyzed by transmission electron microscopy (TEM & HRTEM, JEM2010-HR). The ultraviolet (UV)-visible diffuse reflectance spectra were measured using a UV-visible spectrophotometer (DRS, UV2450) with an integrating sphere attachment. The photoluminescence properties were characterized by a combined fluorescence lifetime and steady state spectrometer (PL, FLSP920) with a xenon lamp (excitation wavelength 350 nm) as a light source. Photocurrents were measured by an electrochemical analyzer (CHI660E Instruments) in a standard three-electrode system with the as-prepared samples as the working electrodes with an active area of approximately 0.5 cm^2 , a Pt wire as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode. A 300-W Xe lamp equipped with a UV reflector ($\lambda = 300\text{--}400$ nm, optical power density is 200 mW/cm^2) was used as the UV-light source. N_2 -saturated 0.1

mol/L NaOH in water was used as the electrolyte.

2.3. Photocatalytic activity evaluation

Photocatalytic degradation of toluene over the as-prepared catalysts was performed in a stainless-steel reactor with a quartz window on the top of the reactor. The reaction vessel was evacuated and backfilled with a gas mixture of O₂, N₂ (O₂:N₂ = 1:3) and trace toluene. Vaporous toluene was injected by flowing the simulated air into a saturator that was filled with toluene solution before entering the vessel. Prior to visible-light irradiation, the reaction vessel was kept in the dark for 2 h until an adsorption-desorption equilibrium was established. The initial concentration of gaseous toluene was ~500 ppm, and the relative humidity in the reactor was approximately 16%. The light source was a 300-W Xe lamp equipped with a UV reflector ($\lambda = 300\text{--}400$ nm, optical power density is 200 mW/cm²). An aliquot of 0.2 g catalyst powder was suspended in deionized water to disperse in a quartz reaction vessel with an irradiation area of 7.0 cm², and then dried at 70 °C in air overnight before photocatalytic test. The photocatalytic reaction was typically carried out under atmospheric pressure at room temperature for 120 min. The atmospheric composition in the reaction vessel was analyzed with a gas chromatography system (GC7900, Tianmei, China), which was equipped with a flame ionization detector (FID). The CO₂ formation amount was measured by

another gas chromatograph (GC2060, FID) equipped with a nickel catalyst-based methanizer with a flame ionization detector. The performance of the photocatalyst was evaluated by the CO₂ formation rate, and the removal of toluene was calculated by using the following equation:

$$\text{Conversion} = (n_{\text{CO}_2,t}/7)/n_{\text{tol},0} \times 100\% \quad (1)$$

where $n_{\text{tol},0}$ is the initial molar quantity of gaseous toluene in the reactor, and $n_{\text{CO}_2,t}$ is the gaseous CO₂ molar quantity at irradiation time (t).

3. Results and discussion

3.1. Structural properties

Fig. 1(a) displays the XRD patterns of commercial P25 and ZnO/P25 samples calcined at 500 °C with different ZnO loadings. As presented, commercial P25 contains both the tetragonal anatase structured TiO₂ (JCPDS 21-1272) and tetragonal rutile TiO₂ (JCPDS 21-1276). For the ZnO/P25-500 samples, except for the characteristic peaks assigned to ATiO₂ and RTiO₂, the hexagonal zincite phase (ZnO, JCPDS 36-1451) is detected, and the intensity of its characteristic peaks increases with the increase in the ZnO loading. Since the phase transform from anatase to rutile may happen upon calcination [27,28], the relative amount of ATiO₂ and RTiO₂ in the samples was estimated by calculating the diffraction peak intensity ratio I_A/I_R of ATiO₂

Fig. 1. XRD patterns of ZnO/P25 composites calcined at 500 °C with different ZnO loads (a) and 0.5% ZnO/P25 calcined at different temperatures (c); the corresponding diffraction peak intensity ratios of ATiO₂ ($2\theta = 25.3^\circ$) to RTiO₂ ($2\theta = 27.4^\circ$) in these samples (b, d). The pattern of P25 is listed as a reference.

($2\theta = 25.3^\circ$) to RTiO_2 ($2\theta = 27.4^\circ$). As presented in Fig. 1(b), the I_A/I_R values of the $\text{ZnO}/\text{P25-500}$ samples are all close to that of P25, indicating no obvious phase change in the P25 support occurs upon ZnO loading and the subsequent calcination at 500 °C. Fig. 1(c) shows the XRD patterns of 0.5%ZnO/P25 calcined at different temperatures, and Fig. 1(d) is the corresponding relationship between the I_A/I_R values and the calcination temperature of the 0.5%ZnO/P25 samples. As presented, these samples all consist of ATiO_2 , RTiO_2 and ZnO phases, and no obvious change in their composition can be detected when the calcination temperature increases from 300 to 500 °C. However, at a high calcination temperature of 700 °C, a serious phase change from ATiO_2 to RTiO_2 proceeds, and a little ATiO_2 can be detected in 0.5%ZnO/P25-700.

The BET surface area, average pore size and pore volume of commercial P25 and 0.5%ZnO/P25 calcined at different temperatures are listed in Table 1. As shown, upon loading of 0.5%ZnO and calcining at 300 °C, the pore volume and pore size of 0.5%ZnO/P25-300 are larger than those of the commercial P25 powder. This phenomenon is probably because of the crystallization of the amorphous phase in P25 during this process, which may open (or create) some plugged pores along with the blockage of the small pores by the Zn species and sintering. As a result, no obvious BET-area change between P25 and 0.5%ZnO/P25-300 is observed. The existence of the minor amorphous phase aside from the main ATiO_2 and RTiO_2 in P25 was demonstrated previously by Ohtani et al. [29]. Both the BET-area and pore volume of 0.5%ZnO/P25 decrease with further increasing calcination temperature, which is more remarkable for 0.5%ZnO/P25-700. The serious sintering in 0.5% ZnO/P25-700 upon calcinating at 700 °C relates to the transformation from the anatase to rutile phase [28,30]. Amores et al. [30] proposed that the time needed for the sintering of the rutile particles produced by the anatase phase transformation was shortened owing to the heat produced by the phase transformation itself, which they termed as ‘phase transformation-induced sintering’. TEM and HRTEM images of 0.5%ZnO/P25-500 are displayed in Fig. 2. As shown, 0.5%ZnO/P25-500 is mainly composed of irregular nanoparticles with a diameter of 20–50 nm. HRTEM image in Fig. 2(b) clearly shows that the sample is composed of ATiO_2 , RTiO_2 and ZnO phases, and the heterojunction structure among the anatase (101), rutile (110) and ZnO (002) is formed.

Table 1

BET surface area (A), average pore size (D) and pore volume (V) of samples.

Sample	A (m^2/g)	D^a (nm)	V^b (cm^3/g)
P25	55	12.0	0.17
0.5%ZnO/P25-300	55	24.7	0.44
0.5%ZnO/P25-500	39	24.3	0.41
0.5%ZnO/P25-700	9	35.2	0.11

^aBJH desorption average pore width. ^bBJH desorption pore volume for the 1.7–300 nm range of pore diameters.

3.2. Optical properties

Fig. 3 presents the UV-vis diffuse reflectance spectra (DRS) of P25 and ZnO/P25 with various ZnO loadings and calcination temperatures, which show the photo-absorption in the UV light region for all the samples. Generally, the loading of ZnO enhances the photo-absorption of P25. Among these samples, 0.5%ZnO/P25-500 holds the strongest photo-absorption. The optical band gaps (E_g) of the samples can be estimated by using the following equation [31]:

$$\alpha h\nu = C(h\nu - E_g)^n \quad (1)$$

Herein, $h\nu$ is the photon energy, α is the absorption coefficient, and C is a constant. n is determined by the type of optical transition of the semiconductor and also depends on the polymorph (i.e., $n = 1/2$ for direct transition and $n = 2$ for indirect transition). Here, we used $n = 2$ for all the samples. The optical band gap values, estimated from the insets in Fig. 3(a) and (b), are shown in Table 2. As shown, a slight red shift to the visible-light region is observed for these ZnO/P25 samples in comparison with the band gap of P25 (3.16 eV). In addition, the shift value increases with an increase of the calcination temperature. Because the phase transformation from ATiO_2 to RTiO_2 in the composites is more serious at a high temperature and the band gap of RTiO_2 is narrower than that of ATiO_2 , the red shift in the ZnO/P25 composites is expected with an increase of the calcination temperature.

PL spectra are regarded as an effective approach to evaluate the separation efficiency of the photo-induced carriers [32]. As seen in Fig. 4(a) and (b), the emission centered at 468 nm is attributed to the radiative recombination of a hole in the valence band and an electron in the conduction band (near band emission, NBE). As shown, the NBE peak intensity of all the

Fig. 2. TEM (a) and HRTEM (b) images of 0.5% ZnO/P25-500.

Fig. 3. UV-vis diffuse reflectance spectra of ZnO/P25 composites calcined at 500 °C with various ZnO loadings (a) and 0.5%ZnO/P25 calcined at various temperatures (b). Insets show the dependence of $(\alpha h\nu)^2$ on the photon energy.

ZnO/P25 samples is clearly lower than that of P25, among which the peak of 0.5%ZnO/P25-500 is the lowest. These results indicate that the modification of P25 by minor ZnO can efficiently improve the photo-induced charge separation, and this improvement is more prominent in 0.5%ZnO/P25-500. Photo-electrochemical properties of P25 and 0.5%ZnO/P25-500 thin films were further used to detect their transient photocurrent responses and the electron-hole separation and transfer difference. The photocurrent (I)-time (t) responses of P25 and 0.5%ZnO/P25-500 with several on-off cycles under UV light irradiation are shown in Fig. 4(c). As indicated, both samples generate photocurrents with a reproducible response to on-off cycles under UV light irradiation, demonstrating the

effective charge transfer and electron collection for the photo-electrodes. The photocurrent density of 0.5%ZnO/P25-500 is approximately 210 $\mu\text{A}/\text{cm}^2$, which is considerably larger than that of P25 ($\sim 78 \mu\text{A}/\text{cm}^2$). The obvious photocurrent enhancement of 0.5%ZnO/P25-500 indicates more efficient UV light absorption and separation of photo-induced electrons/holes of the charge carrier at the interface, which is consistent with the DRS and PL analysis above. Moreover, there is no obvious decrease in the photocurrent density after 4 cycles of on-off UV exposure, indicating the good stability of the 0.5%ZnO/P25-500 photo-electrode.

3.3. Photocatalytic performance

The as-synthesized samples were then evaluated for the photocatalytic degradation of toluene in a batch reactor under UV irradiation ($\lambda = 300\text{--}400 \text{ nm}$). Fig. 5(a) shows that all the ZnO/P25 samples calcined at 500 °C can completely convert toluene into CO_2 after UV-light illumination for 2 h, and 0.5%ZnO/P25-500 exhibits the highest photocatalytic degradation rate. As a reference, the performance of P25 powder after the same calcination process is also provided in Fig. 5(a), which shows a significantly lower photocatalytic degradation rate than that of 0.5%ZnO/P25-500.

Table 2

Estimated band gap values of commercial P25, ZnO and ZnO/P25 heterojunctions with various ZnO loadings and calcination temperatures.

Sample	E_g/eV
P25	3.16
ZnO	3.10
0.1%ZnO/P25-500	3.08
0.5%ZnO/P25-300	3.08
0.5%ZnO/P25-500	3.04
0.5%ZnO/P25-700	2.95
1.0%ZnO/P25-500	3.06

Fig. 4. PL spectra of ZnO/P25 composites calcined at 500 °C with various ZnO loadings (a) and 0.5%ZnO/P25 calcined at various temperatures (b); Time-dependent photocurrents of P25 and 0.5%ZnO/P25-500 electrodes under an on-off UV exposure pulse of 100 s ($\lambda \leq 400 \text{ nm}$) (c).

Fig. 5. UV-light photocatalytic decomposition of toluene over different catalysts at 30 °C. (a) ZnO/P25 composites calcined at 500 °C with various ZnO loadings; (b) 0.5% ZnO/P25 calcined at various temperatures; (c) Commercial P25, 0.5%ZnO/P25-500 and blank test without photocatalyst; (d) Cyclic stability test of 0.5%ZnO/P25-500; (e,f) Adsorption of toluene over commercial P25 and 0.5%ZnO/P25-500 at 30 °C without light illumination.

Fig. 5(b) displays the toluene decomposition rate over 0.5%ZnO/P25 calcined at various temperatures. As shown, 0.5%ZnO/P25-500 shows higher photocatalytic activity than the 0.5%ZnO/P25 samples calcined at 300 and 700 °C. The performance of 0.5%ZnO/P25-500 and commercial P25 was compared. As shown in Fig. 5(c), 0.5%ZnO/P25-500 presents a higher toluene conversion efficiency in comparison with P25, with a ~100% toluene conversion over 0.5%ZnO/P25-500 in comparison with ~90% over P25 after irradiation for 80 min. Besides, no obvious toluene degradation was observed under UV-light without a photocatalyst present during the 2-h reaction time, indicating that the gaseous toluene degradation can be ignored. To make a quantitative photocatalytic activity comparison among these samples, the reaction process was

analyzed using pseudo-first order reaction kinetics, and the corresponding reaction rate constant was regressed from the $\ln(C_0/C_t)$ versus t plot for each sample, as plotted in the insets of Fig. 5(a–c). The as-regressed reaction rate constants for 0.5%ZnO/P25-500 and P25 are 0.051 ($R^2 = 0.99$) and 0.031 min^{-1} ($R^2 = 0.99$), respectively, indicating the higher degradation rate of 0.5%ZnO/P25-500.

The cyclic stability of 0.5%ZnO/P25-500 is shown in Fig. 5(d), and there is no obvious decrease in toluene conversion after UV-light irradiation for 2 h over 3 cycles, indicating the good stability of 0.5%ZnO/P25-500. Finally, the toluene adsorption curves over commercial P25 and 0.5%ZnO/P25-500 were measured under the same initial toluene concentration used in the photocatalytic evaluation experiments at 30 °C as a

reference, and are shown in Fig. 5(e) and (f). The equilibrium toluene adsorption amount over commercial P25 is approximately 0.35 mg/g and is approximately 0.27 mg/g over 0.5%ZnO/P25-500.

3.4. Discussion

When minor ZnO is loaded over P25, the heterojunction is formed, which may reduce the recombination probability of photo-induced electrons and holes by the internal electric field and thus lead to a high quantum yield. The photo-induced charges separation efficiency strongly depends on the band-edge positions of the two semiconductors. The conduction band (CB) and valence band (VB) potentials of ZnO and P25 at the point of zero charge can be calculated by the following empirical equation [33]:

$$E_{VB} = X - E^e + 0.5E_g \quad (2)$$

where E_{VB} is the VB edge potential, X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms. Herein, the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy, rather than the common definition of the term. E^e is the energy of free electrons on the hydrogen scale (~ 4.5 eV), E_g is the band gap energy of the semiconductor, and E_{CB} can be determined by $E_{CB} = E_{VB} - E_g$. The X values for ZnO and P25 are approximately 5.67 and 5.83 eV, respectively [34]. Using the equation above, the top valence band and the bottom conduction band were calculated to be 2.72 and -0.38 eV for ZnO, and 2.91 and -0.25 eV for P25, respectively.

Because both ZnO and P25 can be excited by UV light, the photocatalytic reaction can be initiated by the absorption of UV-light photons with energy equal to or higher than the band gap, resulting in the creation of photo-induced holes in the VB and electrons in the CB in both ZnO and P25. According to the band-edge position, the photo-induced electrons in the CB of ZnO can be easily transferred to that of P25, and the simultaneous holes in the VB of P25 can be transferred to that of ZnO under induction by the internal electric field (Scheme 1). Hence, most of photo-induced electrons and holes are spatially separated from each other, leading to an increased lifetime of the charge carriers and an enhanced interfacial charge transfer

to adsorbed organic molecules [14], which is consistent with the optical characterization analysis presented above. These separated electrons in the CB of both ZnO and P25 can reduce the oxygen adsorbed on the photocatalyst to $\text{HOO}^\bullet$ because the CB minimum is located at a more negative potential ($-0.38/-0.25$ eV) than the electrochemical potential of the desired reaction ($\text{O}_2/\text{HOO}^\bullet = -0.05$ eV, $\text{O}_2/\text{O}_2^{\bullet-} = -0.33$ eV) [35]. While the separated holes in the VB maximum of both ZnO (2.72 eV) and P25 (2.91 eV) can oxidize either the pollutant directly or hydroxyl/water to produce $\text{OH}^\bullet$ radicals with oxidation potentials ($\text{OH}^\bullet/\text{OH}^- = 1.89$ eV, $\text{OH}^\bullet/\text{H}_2\text{O} = 2.72$ eV) [36]. All these $\text{HOO}^\bullet$, $\text{OH}^\bullet$ and holes can participate in the photocatalytic reactions to decompose organic compounds, such as toluene, which leads to the enhanced photocatalytic activity of 0.5%ZnO/P25-500 in comparison with P25. Actually, P25 is composed of ATiO_2 and RTiO_2 , and ZnO/ ATiO_2 / RTiO_2 junctions are formed in ZnO/P25 (Fig. 2). The band-edge positions and the proposed electron-hole pair separation of ZnO/ ATiO_2 / RTiO_2 heterojunctions are also shown in Scheme 1. Here, the E_g values of ATiO_2 (~ 3.20 eV) and RTiO_2 (~ 3.03 eV) were taken from the literature [37]. Owing to the difference in the CB and VB positions among these three phases, photo-induced electrons and holes are spatially separated from each other efficiently. Photo-induced holes on the VB of ATiO_2 can transfer to the VB of ZnO and RTiO_2 , and the photo-induced electrons on the CB of ZnO can transfer to the CB of ATiO_2 and RTiO_2 . The multichannel electrons/holes transfer and separation formed in the ZnO/ ATiO_2 / RTiO_2 heterojunctions leads to the efficient photo-induced charge separation in ZnO/P25.

This proposed multichannel charge separation process and its promotion to the performance of ZnO/P25 heterojunctions can well explain the results obtained in this work. Although the BET surface area and equilibrium toluene adsorption amount of commercial P25 ($55 \text{ m}^2/\text{g}$ and ca. 0.35 mg/g) are higher than those of 0.5%ZnO/P25-500 ($39 \text{ m}^2/\text{g}$ and ca. 0.27 mg/g), the photocatalytic activity of 0.5%ZnO/P25-500 developed in this work is still high, indicating that the multichannel charge separation promotion effect prevails. Generally speaking, the crystallinity and the interaction among the composed phases can be improved at a high calcination temperature, which is beneficial for charge separation. Thus, the PL spectra of 0.5%ZnO/P25 calcined at various temperatures (Fig. 4(b)) indicate the better

Scheme 1. Diagram for the band levels and the proposed electron-hole pair separation of ZnO/P25 heterojunctions.

charge separation in 0.5%ZnO/P25-500 than that of 0.5%ZnO/P25-300. However, when the calcination temperature was raised to 700 °C, a poorer charge separation over 0.5%ZnO/P25-700 than that over 0.5%ZnO/P25-500 was observed. Owing to the almost complete transformation from ATiO_2 to RTiO_2 and from the triple-phase $\text{ZnO}/\text{ATiO}_2/\text{RTiO}_2$ junctions to the dual-phase ZnO/RTiO_2 junctions, the multichannel charge separation in 0.5%ZnO/P25-700 is suppressed, leading partly to its lower quantum yield and photocatalytic activity compared with that of 0.5%ZnO/P25-500. The loading of ZnO also exerts an important effect on the formation and function of the $\text{ZnO}/\text{ATiO}_2/\text{RTiO}_2$ heterojunctions. With an appropriate ZnO loading, that is, 0.5%ZnO/P25-500, the as-formed $\text{ZnO}/\text{ATiO}_2/\text{RTiO}_2$ heterojunctions and multichannel charge separation process can effectively improve the charge separation and the photocatalytic performance of the ZnO/P25 composite. In the case of the catalyst with a high amount of ZnO, that is, 1.0%ZnO/P25-500, the properties of bulk ZnO may dominate the surface properties of the ZnO/P25 composite, and the promotion to the charge separation and photocatalytic performance by the surface heterojunctions is suppressed. Kim et al. [21] also reported that the photocatalytic properties decreased as the thickness of the ZnO layer increased in the ZnO/TiO₂ nanoporous films. In contrast, lower amounts of ZnO cannot effectively modify the P25 surface to form effective heterojunctions. These aspects suggest that the optimum ZnO addition amount to enhance the properties of ZnO/P25-500 is around 0.5 wt%. Therefore, we can see that the modification of P25 by minor ZnO can effectively improve the photo-induced charge separation and photocatalytic properties of toluene degradation by the formation of $\text{ZnO}/\text{ATiO}_2/\text{RTiO}_2$ heterojunctions and multichannel electron/hole transfer and separation.

4. Conclusions

ZnO/P25 composites were synthesized by a facile incipient wetness impregnation method and evaluated for the photocatalytic removal of gaseous toluene. The ZnO/P25 composites consist of anatase TiO₂ (ATiO_2), rutile TiO₂ (RTiO_2) and hexagonal zincite structures. The parasitic phase of ZnO in P25 led to the formation of $\text{ZnO}(002)/\text{ATiO}_2(101)/\text{RTiO}_2(110)$ heterojunctions and enhanced light absorption. The multichannel

electron/hole separation in the as-formed heterojunctions remarkably improved the photo-induced charge separation. Toluene was completely oxidized into CO₂ over ZnO/P25 composites under UV light irradiation ($\lambda \leq 400$ nm) and ambient temperature. In comparison with commercial P25, 0.5%ZnO/P25 calcined at 500 °C showed remarkably enhanced photocatalytic activity owing to the effective electron-hole separation at the interfaces of the heterojunctions. Hence, the modification of P25 by minor ZnO can efficiently improve the photo-induced charge separation and photocatalytic properties for toluene degradation by the heterojunctions formation and multichannel electron/hole transfer and separation.

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Graphical Abstract

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Multichannel charge separation promoted ZnO/P25 heterojunctions for the photocatalytic oxidation of toluene

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The parasitic phase of ZnO in P25 leads to the formation of $\text{ZnO}(002)/\text{ATiO}_2(101)/\text{RTiO}_2(110)$ heterojunctions. This multichannel electron/hole separation in the as-formed heterojunction remarkably improves the photoinduced charge separation and its photocatalytic performance.

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具有多通道载流子分离功能的 ZnO/P25 异质结构光催化氧化甲苯

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摘要: 甲苯是一种最常见的室内有毒挥发性有机物 (VOCs), 目前消除方法主要有吸附、催化燃烧和光催化氧化, 其中光催化是一种最高效和经济可行的方法, 能在较温和条件下将甲苯完全矿化为 CO₂。作为研究最广泛的光催化剂, TiO₂ 在应用中通常有锐钛矿 (ATiO₂) 和金红石 (RTiO₂) 两种物相, 但单相 TiO₂ 的低量子产率和光生电子-空穴对的快速复合严重限制了它的应用。本文选择兼具锐钛矿和金红石两种物相的 P25 为催化剂载体, 通过负载少量 ZnO 和构建多组分并具备多通道载流子分离功能的异质结以提高 TiO₂ 基光催化剂的性能。

利用一步浸渍法制备了一系列 ZnO/P25 复合光催化剂, 考察了其光催化降解气相甲苯性能。X 射线粉末衍射结果表明, ZnO/P25 异质光催化剂是由 ATiO₂, RTiO₂ 和红锌矿三种物相结构组成。高分辨透射电镜结果表明, ZnO/P25 具备三相异质结 ZnO(002)/ATiO₂(101)/RTiO₂(110)。紫外可见光谱、荧光光谱和光电流表征结果表明, ZnO/P25 所形成的三相异质结不但增强了光吸收能力, 还实现了多通道电子/空穴分离。催化降解实验表明, ZnO/P25 异质光催化剂能在室温紫外光辐射下将甲苯完全矿化为 CO₂ 和 H₂O。基于三相异质结和多通道光生电子-空穴对分离的形成及促进作用, ZnO/P25 光催化活性和速率均明显高于 P25。本文报道的多通道载流子分离理念可为高效光催化剂设计和应用提供一种新思路。

关键词: 二氧化钛; 氧化锌; 甲苯; 光催化; 异质结; 多通道载流子分离

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