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Article

Time-resolved photoluminescence of anatase/rutile TiO₂ phase junction revealing charge separation dynamics

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ABSTRACT

Junctions are an important structure that allows charge separation in solar cells and photocatalysts. Here, we studied the charge transfer at an anatase/rutile TiO₂ phase junction using time-resolved photoluminescence spectroscopy. Visible (~500 nm) and near-infrared (NIR, ~830 nm) emissions were monitored to give insight into the photoinduced charges of anatase and rutile in the junction, respectively. New fast photoluminescence decay components appeared in the visible emission of rutile-phase dominated TiO₂ and in the NIR emission of many mixed phase TiO₂ samples. The fast decays confirmed that the charge separation occurred at the phase junction. The visible emission intensity from the mixed phase TiO₂ increased, revealing that charge transfer from rutile to anatase was the main pathway. The charge separation slowed the microsecond time scale photoluminescence decay rate for charge carriers in both anatase and rutile. However, the millisecond decay of the charge carriers in anatase TiO₂ was accelerated, while there was almost no change in the charge carrier dynamics of rutile TiO₂. Thus, charge separation at the anatase/rutile phase junction caused an increase in the charge carrier concentration on a microsecond time scale, because of slower electron-hole recombination. The enhanced photocatalytic activity previously observed at anatase/rutile phase junctions is likely caused by the improved charge carrier dynamics we report here. These findings may contribute to the development of improved photocatalytic materials.

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1. Introduction

Inorganic heterojunctions are an important structure for enhancing photoinduced charge separation in a range of materials and devices, including solar cells [1] and photocatalysts [2–4]. The tracking of charge transfer dynamics at such heterojunctions is crucial to guide future materials design. In this work, we used time-resolved photoluminescence to study mixed phase TiO₂ samples with a mixture of anatase and rutile phases, which formed an inorganic heterojunction. We focused in particular on the photoinduced charge transfer between the

two phases and its impact on charge recombination.

Titanium dioxide (TiO₂) is among the most well-studied semiconductor photocatalysts owing to its unique physicochemical properties. The two major crystalline structures of TiO₂ photocatalysts are anatase and rutile, which have band gaps of 3.2 and 3.0 eV, respectively. The crystalline structure of TiO₂ has a great impact on its photocatalytic performance. Anatase is regarded as the most active phase for photocatalytic reactions [5,6] such as photodegradation of environmental pollutants [7], while rutile is reported to be more active than anatase for photocatalytic water oxidation and overall water

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splitting [8,9]. Mixed phase TiO₂ that contain anatase/rutile heterojunctions are also more active than pure anatase or rutile phases in photodegradation of organic contaminants [10] and in photocatalytic H₂ production [11,12]. This enhanced photocatalytic activity has been attributed to efficient charge separation and reduced charge recombination at anatase/rutile phase junctions.

Charge transfer at an anatase/rutile inorganic heterojunctions has been extensively studied theoretically and experimentally. The majority of previous research has focused on electron transfer processes. Electron transfer from rutile to anatase has been studied by electron paramagnetic resonance (EPR) [13], surface photovoltage spectroscopy (SPV) [14], time-resolved terahertz spectroscopy [15], and solid-state NMR spectroscopy [16], supported by the band alignment of anatase and rutile determined in a recent X-ray photoelectron spectroscopy (XPS)/modeling study [17,18]. Electron transfer from anatase to rutile has also been studied using transmission electron microscopy (TEM) [19], EPR [20], SPV [21], and time-resolved mid-infrared spectroscopy [22], in accordance with the higher conduction band minimum of anatase than that of rutile calculated by Kang et al. [23]. Recently, Mi et al. [24] proposed that the electron migration direction is also controlled by dynamic factors, such as the anatase particle size and the presence of electron or hole scavengers.

Hole transfer at an anatase/rutile phase junction has also been investigated by time-resolved spectroscopy. Carneiro et al. [25] proposed that positive charges become trapped at the rutile surface based on results from time-resolved microwave conductance measurements. Hole transfer from rutile to anatase was demonstrated by transient absorption spectra, focusing on the carrier dynamics at μs -ms time scales [26]. Although many aspects of the charge transfer dynamics at anatase/rutile heterojunctions in TiO₂ have been investigated, certain kinetic aspects of the charge transfer require further confirmation. A full understanding of the charge separation and recombination processes at these heterojunctions may lead to improved photocatalytic materials.

In this work, pure anatase and pure rutile TiO₂, and mixed phase TiO₂ samples with anatase/rutile phase junction were studied by time-resolved photoluminescence (PL). PL spectroscopy is a powerful technique for studying the recombination dynamics of semiconductor photocatalysts. In particular, PL spectroscopy is useful for investigating charge transfer processes in composite photocatalysts systems, by analyzing changes in PL intensities and lifetimes. The occurrence of charge transfer at anatase/rutile heterojunctions was confirmed from the appearance of new fast-decay components in our PL lifetime measurements. Charge separation is improved on the microsecond time scale at the anatase/rutile junction, which resulted in a high charge carrier density and slower charge carrier recombination on a microsecond time scale.

2. Experimental section

2.1. Synthesis of mixed phase TiO₂ with anatase/rutile heterojunction

TiO₂ was prepared by a precipitation method [27]. Titanium(IV) *n*-butoxide (Ti(OBu)₄; 40 mL) was added to 200 mL of anhydrous ethanol. The resulting solution was then added to a 200-mL mixture of deionized water and anhydrous ethanol (4:1, V/V). The molar ratio of water/Ti(OBu)₄ in the resulting mixture was 75/1. After continuous stirred for 24 h, a white precipitate was formed, which was then filtered and washed twice with deionized water and anhydrous ethanol. Finally, the samples were dried at 100 °C and then calcined at high temperature in air for 2 h. The samples calcined at temperature *T* °C, are indicated from here onwards as TiO₂-*T*. The TiO₂ samples calcined at 500 and 900 °C were also characterized as pure anatase and pure rutile, respectively.

2.2. Preparation of mechanically mixed phase TiO₂

The anatase and rutile TiO₂ samples were mechanically mixed at a given weight ratio and ground to ensure sufficient mixing. The samples were named as A-R 3-1, A-R 9-1 and A-R 19-1 with anatase:rutile ratios of 3:1, 9:1 and 19:1, respectively.

2.3. Synthesis of anatase/rutile mixed phase TiO₂ with controlled phase composition

Degussa P25 (rutile fraction about 12%, as estimated from the integrated rutile (1 1 0) and anatase (1 0 1) XRD peak intensities) was used to prepare mixed phase TiO₂ with a controlled phase composition by a thermal treatment [11]. The obtained TiO₂ was denoted as P25-*x*%R, where *x* indicates the rutile content estimated from XRD measured by the equation:

$$x = \frac{1}{1 + 0.884 \left(\frac{A_{\text{ana}}}{A_{\text{rut}}} \right)}$$

where *A*_{ana} and *A*_{rut} are the integrated intensities of the anatase (101) and rutile (110) XRD peaks, respectively. These photocatalysts are referred as P25-100% R-a,c where a and c indicate different treatment conditions. The proportion of rutile phase in these structures was tuned by changing the calcination temperature and calcination time [11].

2.4. Preparation of cryogenic TiO₂ samples

A 6-mg portion of TiO₂ was suspended in water (1 mL) and sonicated for 15 min. A 200- μL portion of this suspension was dropped onto a round 1.5 cm diameter quartz disk and allowed to dry slowly in air. In this way TiO₂ films on quartz substrates were obtained.

2.5. Photoluminescence spectroscopy measurements

Photoluminescence spectra were measured with a home-built luminescence spectrograph. The luminescence signal was collected with an ellipsoidal collecting mirror and focused onto a 320 mm monochromator (Jobin-Yvon Triax 320). A Jobin-Yvon Spectrum One CCD 3000 was mounted to detect the luminescence signal. The wavelength calibration of this setup was performed with a mercury lamp prior to the PL

measurements. A continuous He-Cd laser ($\lambda = 325$ nm) was used as the excitation source to measure steady-state PL spectra. All laser-induced PL measurements were performed in air at room temperature. It should be noted that fringes in the NIR region of the spectrum originated from an etaloning effect of the back-illuminated CCD.

The cryogenic photoluminescence spectra were measured in a FLS920 fluorescence spectrometer (Edinburgh Instruments). A 450 W Xe lamp was used as the excitation source for the steady-state PL spectra. Time-resolved photoluminescence spectra were collected with excitation from a μ F920 microsecond flash lamp with a pulse width of ~ 2 μ s. Low-temperature experiments with the TiO₂ samples were performed inside a variable temperature Oxford cryostat model OptistatDN (–196 to 227 °C). The PL decay data were fitted by multiple exponential decays.

2.6. Analytical methods

Powder X-ray diffraction (XRD) patterns were measured with a Rigaku MiniFlex diffractometer with a Cu- K_{α} radiation source. The angular range of the patterns was from 20° to 80° with a step size of 0.02° and a scanning speed of 5°/min. UV Raman spectra were measured on a home-assembled UV Raman spectrograph using a Jobin-Yvon T64000 triple-stage spectrograph with spectral resolution of 2 cm^{–1}. The laser line at 325 nm of a He-Cd laser was used as the exciting light. The phase compositions were estimated by a previously reported method [28].

3. Results

3.1. Steady-state photoluminescence characteristics of TiO₂ with different phase compositions

A range of TiO₂ samples with various bulk and surface crys-

Table 1

TiO₂ samples with various bulk and surface crystalline phases.

Sample	Bulk ^a	Surface layer ^b	Laser-induced PL
TiO ₂ -500	100% A	100% A	Visible Band
TiO ₂ -550	95% A + 5% R ^c	100% A	Visible Band
TiO ₂ -750	26% A + 74% R	96% A + 4% R	Visible + NIR Band
TiO ₂ -800	1% A + 99% R	70% A + 30% R	Visible + NIR Band
TiO ₂ -900	100% R	100% R	NIR Band

^a Phase composition estimated from XRD data.

^b Phase composition estimated from UV-Raman data.

^c A: anatase. R: rutile.

talline phases were prepared. Their structural properties were characterized by XRD and UV-Raman spectroscopy. XRD patterns were used to determine the phase structure of the bulk TiO₂, while UV-Raman spectra were used to reveal the phase structure of the surface layer of the TiO₂ [28]. TiO₂-500 was found to be composed of pure anatase while TiO₂-900 was composed of pure rutile, in both their bulk and surface regions. The TiO₂ samples calcined at temperatures of 550–830 °C were composed of a mixture of phases, and also showed differences in the composition of their bulk and surface crystalline phases. The TiO₂-550, TiO₂-750 and TiO₂-800 samples were selected to study the anatase/rutile phase junction. The phase composition and PL properties of these samples are summarized in Table 1.

TiO₂ samples with various bulk and surface crystalline phases were studied by PL spectroscopy using excitation at 325 nm with a laser (Fig. 1). The emission bands corresponded to previous reports for these TiO₂ phases. Namely, anatase TiO₂ (TiO₂-500) showed an emission at ~ 500 nm, while rutile TiO₂ (TiO₂-900) showed a near-infrared (NIR) luminescence at around ~ 835 nm [27,29]. For TiO₂ samples that were calcined below 700 °C, only a visible luminescence band was observed, which increased in intensity as the calcination temperature was raised. For samples calcined above 700 °C, the intense visible emission band remained, and a weak NIR luminescence band

Fig. 1. (a) Photoluminescence spectra of the TiO₂ samples with different phase compositions; the excitation source was 325 nm. (b) The dependence of the luminescence intensity on the calcination temperature.

was also observed. These results are consistent with the formation of a rutile phase on the surface region of the TiO_2 particles. At higher calcination temperatures the intensity of the visible emission band gradually declined as the NIR luminescence band became more intense (Fig. 1(b)). These results suggest that the TiO_2 surface region underwent further phase transformations. At a calcination temperature of 900 °C, only the NIR luminescence band was observed. The phase structures determined by our PL studies were in good agreement with our UV-Raman results, illustrating that PL is a technique with high surface sensitivity. The visible emission intensity increased as the calcination temperature was increased from 500 to 650 °C; however, the bulk TiO_2 started to transform from anatase to rutile phases above 550 °C. We expected that the visible emission intensity would decrease as the anatase content decreased, owing to the phase transformation of anatase to rutile. The increase of visible emission intensity as the TiO_2 samples' anatase content decreased suggested that charge transfer occurred from rutile to anatase phases. For further increases of the calcination temperature, the visible emission decreased gradually. This resulted in a considerable decrease in the visible intensity of TiO_2 -800 to about half that of TiO_2 -500.

The PL excitation spectra of the TiO_2 samples are shown in Fig. 2. The excitation peak is at ~340 nm for the visible emission of pure anatase, while the excitation peak is at ~390 nm for the NIR emission from rutile [27]. For TiO_2 -550 with only a small amount of rutile in its bulk, the excitation properties were almost the same as those of pure anatase. However, for TiO_2 -750, which featured both anatase and rutile phases, the excitation peak shifted from 340 to 330 nm for the visible emission. Notably, the excitation features of the NIR emission for anatase/rutile TiO_2 remained unchanged. These results suggested that the absorbance of rutile at longer wavelengths was more efficient than that of anatase, indicating that the incorporation of rutile can improve the response of TiO_2 systems

at long wavelengths.

3.2. Time-resolved photoluminescence characteristics of TiO_2 with different phase compositions

The visible emission showed fast (microsecond-time scale, Fig. 3(a)) and slow (millisecond-time scale (Fig. 3(b)) decay components [27]. The presence of the anatase/rutile phase junction affected the fast and slow components of the visible emission differently. For the fast decay component, all the mixed phase TiO_2 samples showed slower decay on the microsecond time scale than that of the pure anatase sample (average lifetimes $\langle \tau \rangle$ are shown in Table 2). This result indicated that the anatase/rutile phase junction can retard carrier recombination on the microsecond-time scale. For the TiO_2 -750 sample, the formation of surface rutile gave the slowest decay with an average lifetime of 30.90 μs . All the decay curves could be fitted by three decay components. We compared the slower components (τ_2 and τ_3), for all the mixed phase TiO_2 samples, and showed that the microsecond-time scale decays were much slower than those of pure anatase. For the fastest component (τ_1), TiO_2 -800 exhibited an accelerated decay (0.43 μs), which was more rapid than that of other samples calcined below 750 °C. Although the particle size and morphology of the TiO_2 particles were altered during the calcination process, the observed change of the visible lifetime on the microsecond time scale could not be attributed to changes of the particle size or particle morphology. The particle size and morphology were only slightly changed in the calcination temperature range 500–550 °C [11,28], while the average PL lifetime increased considerably from 11.50 to 25.60 μs . Furthermore the average PL lifetime did not clearly increase in the calcination temperature range of 550–800 °C; however, the particle size and morphology were altered considerably [11, 28]. Thus, the slower charge carrier recombination of anatase/rutile TiO_2 indicated slower recombination on a microsecond time scale. Moreover, the accelerat-

Fig. 2. Excitation spectra of TiO_2 samples with different phase compositions measured at -196 °C for visible (a) and NIR (b) emissions. The PL signals at 520 and 820 nm were monitored as the visible and NIR emissions, respectively.

Fig. 3. PL decays of TiO₂ samples with different phase compositions in 400 μ s (a) and 20 ms (b) time ranges monitored at 520 nm and at a temperature of -196 $^{\circ}$ C. The excitation source was 340 nm.

ed decay (0.43 μ s) in TiO₂-800 indicated charge transfer from anatase to rutile, because rutile was the dominant phase of this sample. Conversely, on the millisecond-time scale, the mixed phase TiO₂ featured more rapid PL decay, as the rutile phase composition increased, as shown in Fig. 3(b) and Table 3 (by comparing the slower components τ_2 and τ_3). These results indicate that the charge carrier recombination was not slowed by the anatase/rutile phase junction on the millisecond time scale, but accelerated slightly.

The NIR luminescence exhibited fast exponential decay on the microsecond time scale (Fig. 4(a)) and a slow power-law decay on a millisecond time scale (Fig. 4(b)) [27]. Unlike the

visible emission, there was almost no change of the slow (millisecond-time scale) decay component as the proportion of anatase phase increased from TiO₂-900 to TiO₂-750, as shown in Fig. 4(b). However, the fast decay component became slower as the amount of anatase increased, as for the TiO₂-800 and TiO₂-750 samples. This result is also in accordance with the slower charge carrier recombination seen for the visible emission. This result further indicated that the anatase/rutile TiO₂ phase junction can slow charge carrier recombination substantially on a μ s time scale. Notably, the sample TiO₂-750 displayed a new fast-decay component (2.13 μ s) in addition to the exponential and power-law components common of the other samples (inset of Fig. 4(a) and Table 4). This new fast-decay component represented charge transfer from rutile to anatase at anatase/rutile phase junctions.

To further investigate the role of the anatase/rutile phase junction, a range of mixed-phase TiO₂, with high photocatalytic activity and controlled phase compositions, were prepared from Degussa P25 by thermal treatments and then characterized. We observed no notable changes in the visible emission PL decay on a microsecond time scale and the decay was accelerated on the millisecond time scale. In the NIR luminescence of the P25 TiO₂ samples with an anatase/rutile phase junction (i.e., P25-21% R, P25-74% R and P25-100% R-a), a new fast-decay component (2.32 μ s) appeared in addition to the microsecond time scale exponential decay component (Fig. 5 and Table 5). This new decay was particularly clear, in the sample with a relative content of 22.05%, P25-74% R. This fast decay was assigned to charge transfer from rutile to anatase. The overall microsecond-time scale decay became slower as contributions from the new rapid decay component increased. Although the P25-100% R-a sample was composed of pure rutile and prepared at a lower temperature than that of P25-100% R-c, the new rapid decay also appeared, and the microsecond-time scale decay became slower. Thus, the fast

Table 2

Exponential fitting results of visible emission decay on 400 μ s time scale in TiO₂-T samples.

Sample	τ_1/μ s	τ_2/μ s	τ_3/μ s	χ^2	$\langle\tau\rangle/\mu$ s
TiO ₂ -500	1.67 (54.35%)	10.30 (32.73%)	55.89 (12.92%)	1.289	11.50
TiO ₂ -550	2.34 (33.74%)	14.49 (35.52%)	63.98 (30.74%)	1.222	25.60
TiO ₂ -750	2.03 (27.62%)	14.96 (34.96%)	66.84 (37.57%)	1.794	30.90
TiO ₂ -800	0.43 (57.79%)	15.53 (15.28%)	72.63 (26.93%)	1.280	22.18

Table 3

Exponential fitting results of visible emission decay on 20 ms time scale in TiO₂-T samples.

Sample	τ_1/μ s	τ_2/μ s	τ_3/μ s	χ^2
TiO ₂ -500	19.46 (46.44%)	187.67 (28.04%)	1544.74 (25.53%)	1.294
TiO ₂ -550	25.36 (64.76%)	137.00 (27.25%)	1561.26 (7.99%)	1.393
TiO ₂ -750	25.63 (53.31%)	118.17 (40.04%)	1305.03 (6.64%)	1.377
TiO ₂ -800	13.71 (50.06%)	74.60 (40.73%)	400.52 (9.21%)	1.026

Fig. 4. PL decays of TiO₂ samples with different phase compositions in 400 μ s (a) and 20 ms (b) time ranges monitored at 820 nm. The excitation source was 390 nm and the temperature was -196 °C. The inset in (a) is the magnification of the initial decay of TiO₂-750.

decay improved the charge separation processes and resulted in overall slower recombination processes in TiO₂ with anatase/rutile phase junctions on the microsecond time scale. There was also no change in the charge carrier recombination on a millisecond time scale.

To confirm that charge transfer occurred at the ana-

tase/rutile phase junction, we mechanically mixed TiO₂ in various anatase/rutile ratios (Fig. 6). At an anatase:rutile ratio of 1:1, the carrier dynamics of the mechanically mixed TiO₂ were almost the same as those of pure anatase and rutile TiO₂. For mechanically mixed TiO₂ with rutile as the dominant component (e.g., anatase:rutile = 1:4), a slightly accelerated decay of the visible emission was observed. This faster decay indicated charge transfer from anatase to rutile. With anatase as the main

Table 4

Fitting results of NIR luminescence decay on 400 μ s time scale for TiO₂-T samples.

Sample	τ_1/μ s	τ_2/μ s	χ^2	$\langle\tau\rangle/\mu$ s
TiO ₂ -750	2.13 (0.80%)	124.14 (99.20%)	1.226	123.16
TiO ₂ -800	—	83.25 (100%)	1.161	83.25
TiO ₂ -900	—	50.70 (100%)	1.324	50.70

Table 5

Fitting results of NIR luminescence decay on 400 μ s time scale for TiO₂ samples prepared from P25.

Sample	τ_1/μ s	τ_2/μ s	χ^2
P25-74% R	2.32 (22.05%)	86.02 (77.95%)	1.438
P25-100% R-a	2.32 (4.00%)	80.87 (96.00%)	1.186
P25-100% R-c	—	40.32 (100%)	1.330

Fig. 5. PL decay curves of the mixed phase TiO₂ samples prepared from P25 monitored at 820 nm, with 390-nm excitation at -196 °C.

Fig. 6. PL decays of mechanically mixed TiO₂ samples monitored at 820 with 390-nm excitation at -196 °C. The anatase/rutile ratios are denoted as A-R.

component (e.g., anatase:rutile = 9:1) a fast decay component also appeared, which was not present in pure rutile (Fig. 6). As the relative anatase content was increased to 19:1, the fast decay became more pronounced. These results also indicated that charge transfer from rutile to anatase occurred. The appearance of the charge transfer, only in TiO_2 which featured either anatase or rutile as the dominant phase indicated poor contact between the mechanically mixed anatase and rutile phases. This poor contact explained the low efficiency of charge transfer and the absence of slowed charge carrier recombination. Thus, charge transfer could take place only when anatase or rutile particles were surrounded by a large amount of dissimilar particles. This result also indicated that the charge transfer was highly dependent on the formation of an anatase/rutile phase junction.

4. Discussion

We compared the PL decay rates of the mixed-phase TiO_2 with those of pure phases [27,29]. The charge transfer process and the effects on charge recombination are illustrated in Scheme 1.

4.1. Charge transfer across anatase/rutile phase junction

On the microsecond time scale, a new fast-decay component with a lifetime of $\sim 2 \mu\text{s}$ was observed for the NIR band in the mixed phase TiO_2 , which indicated charge transfer at the anatase/rutile phase junction. The decay of visible emission was accelerated slightly in the rutile-dominated mixed phase TiO_2 -800. These results illustrated that charge transfer occurred at anatase/rutile phase junctions in mixed phase TiO_2 . Together, the new fast-decay component of the NIR band and the accelerated decay of the visible band indicated that charge transfer occurred from anatase to rutile and from rutile to anatase simultaneously, as shown in Scheme 1(c).

The charge transfer process at the anatase/rutile phase junctions has been previously studied with several characterization techniques, as discussed above. However, previous research has been limited to discussing only a single type of transfer direction; either electron or hole transfer, because only one type carrier, photogenerated electrons or holes, was monitored in these studies. PL measurements allow direct monitoring of the recombination processes of electrons and holes.

Scheme 1. Schematic illustration of charge transfer and recombination at anatase/rutile phase junction.

Electron and hole transfers contribute to changes of the PL decay dynamics. Thus, we demonstrated that charge transfer occurs from rutile to anatase and anatase to rutile, simultaneously. The bidirectional transfer phenomena at the anatase/rutile phase junction are similar to charge transfer processes at a type-II semiconductor heterojunction. Namely, one type of charge carrier transfers from anatase to rutile, while the other transfers from rutile to anatase. The charge transfer direction of specific carrier types cannot be distinguished by PL measurements, but can be studied further by other techniques.

Because changes of electron and hole concentrations affect the intensity and kinetics of PL signals, the dominant charge transfer can be determined from the PL results. Analysis of the PL intensity showed that the visible emission intensity increased relative to that of pure anatase in mixed phase TiO_2 -T ($T < 700^\circ\text{C}$), indicating that the total amount of photo-generated carriers in anatase increased. This result illustrates that charge transfer from rutile to anatase was the dominant pathway. From the kinetic aspects, the new fast-decay component was observed more easily and directly in the NIR emission. The visible band showed only a slight acceleration in rutile-dominated TiO_2 mixtures. For the majority of the mixed phase TiO_2 samples, the new fast-decay component of the NIR band was observed without any acceleration of the visible emission decay. These results further suggest that charge transfer from rutile to anatase is the dominant pathway at the anatase/rutile phase junction. Therefore, charge transfer from rutile to anatase is likely faster and more efficient than the opposite process.

The charge transfer efficiency was highly dependent on the phase contact between anatase and rutile. The mixed-phase TiO_2 samples prepared by calcination exhibited efficient charge transfer processes. However, mechanically mixed TiO_2 samples showed only slight effects; charge transfer was observed when either rutile or anatase was the main component. These results indicated inefficient charge transfer due to poor contact between anatase and rutile particles. Thus, contact between phases should be improved to increase the charge transfer efficiency at anatase/rutile phase junctions.

4.2. Recombination processes in TiO_2 with anatase/rutile phase junction

Next, we discuss the effect of the charge transfer on recombination processes in TiO_2 with anatase/rutile phase junctions. Both the visible and NIR emission bands showed slower decay on the microsecond time scale, when a charge transfer process was observed for the NIR band in TiO_2 -750 and for the visible band in TiO_2 -800. These results indicated that the charge transfer occurred at the anatase/rutile phase junction and can slow the recombination process of photogenerated charge carriers. More importantly, the retardation effect was observed in the visible emission of the TiO_2 -550 samples, where charge transfer from rutile to anatase could not be monitored directly because of the absence of the NIR emission. This retardation demonstrates the existence of an efficient charge transfer from rutile to anatase in the TiO_2 -550 sample, which may explain the

absence of NIR emission, in this, and other mixed phase samples calcined below 700 °C.

No slowing of the charge carrier recombination was observed on a millisecond time scale for the anatase/rutile phase junction TiO₂, although charge transfer slowed the recombination successfully on the microsecond time scale. We observed almost no change for the NIR PL decay on a millisecond time scale with the presence of anatase. However, the decay of the visible emission was accelerated by the presence of rutile on the millisecond time scale, indicating that the photogenerated carrier lifetimes were not prolonged by the anatase/rutile phase junction, but were instead shortened. These results are in good agreement with transient absorption results of anatase/rutile TiO₂ [26], which reported the intermediate half lifetime of holes in anatase/rutile TiO₂. Thus, this work provide further evidence that formation of a anatase/rutile heterojunction can only improve charge separation on microsecond time scale, without slowing the charge carrier recombination on a millisecond-time scale.

4.3. Implications of the PL dynamics for photocatalytic performance

The PL results indicate that charge transfer at an anatase/rutile phase junction can slow recombination efficiently on a microsecond time scale. If photogenerated carriers can be used efficiently on a sub-microsecond- to microsecond- time scale, photocatalytic performance may be considerably enhanced. For photocatalytic proton reduction, using alcohols as hole scavengers, the photo-oxidation of alcohol by photo-induced holes takes place on a sub-microsecond time scale, and results in long-lived electrons with lifetimes of seconds [30,31]. These long-lived electrons may be able take part in further reactions to photo-reduce water to H₂. This may be a key way to improve photocatalytic H₂ production at TiO₂ electrodes composed of mixed anatase/rutile phase TiO₂ [11,32]. Moreover, the charge transfer process increased charge separation, which may allow for generation of more photoinduced electrons and holes. This may allow higher charge carrier concentrations in the anatase phase of mixed anatase/rutile TiO₂. Increasing the amount of photoinduced carriers is another step towards improving photocatalytic activity. Thus, TiO₂ containing anatase/rutile phase junctions may be expected to have enhanced photocatalytic activity for H₂ evolution using alcohols as hole scavengers, and for photodegradation of environmental pollutants.

Unfortunately, the charge recombination was not decreased on a millisecond time scale by the presence of the anatase/rutile phase junction. Thus, photocatalytic reactions that require carriers to have lifetimes longer than a millisecond will not benefit from the formation of anatase/rutile heterojunctions. The PL dynamics suggest that rutile may show a better activity than anatase in slow photocatalytic reactions owing to the longer lifetimes of the NIR luminescence. This may be one factor that contributes to the good photocatalytic performance of rutile in water splitting compared with that of anatase [8].

We compared the PL dynamics of TiO₂ prepared by different

methods and showed that the charge transfer is highly dependent on contact between the anatase and rutile phases. This charge transfer behavior may explain differences in the performance of anatase/rutile TiO₂ materials in previous reports. Thus, improving the contact between phases and making use of sub-microsecond to microsecond time scales are two considerations for use of anatase/rutile phase junction materials in photocatalysis. On the basis of this work, heat treatments at high temperatures were shown to be an effective strategy for improving the phase contact of mixed phase TiO₂.

5. Conclusions

We studied anatase, rutile and anatase/rutile mixed phase TiO₂ samples using time-resolved photoluminescence spectroscopy. The luminescence decay of visible (~500 nm) and NIR (~830 nm) emissions were analyzed to reveal the carrier dynamics in the anatase and rutile TiO₂ phases, respectively. NIR luminescence of samples containing anatase/rutile phase junctions exhibited an additional fast-decay component. Accelerated decay of visible emission occurred in TiO₂ samples with rutile as the main phase. The accelerated luminescence decay indicated the occurrence of charge separation at the anatase/rutile heterojunction. Charge transfer from rutile to anatase was the dominant pathway, as indicated by the increased intensity of the visible emission and the occurrence of new fast-decay component of the NIR band. Photoinduced charge carriers showed slower decay on microsecond-time scales for samples containing the anatase/rutile TiO₂ phase junction, also indicating effective charge separation. However, recombination remained unchanged on a millisecond-time scale. For elementary photocatalytic reactions that occur on the sub-microsecond and microsecond-time scales the use of an anatase/rutile phase TiO₂ junction may improve photocatalytic performance.

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Graphical Abstract

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Time-resolved photoluminescence of anatase/rutile TiO₂ phase junction revealing charge separation dynamics

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Time-resolved photoluminescence results revealed improved charge separation and retarded charge recombination on a microsecond time scale for anatase/rutile TiO₂ phase junctions resulting in enhanced photocatalytic activity.

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锐钛矿/金红石TiO₂相结界面电荷分离的时间分辨发光光谱研究

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摘要: “结”的构筑, 被证实是提高电荷分离效率的重要策略, 在太阳电池、光催化等领域有广泛应用. 跟踪研究异质结、异相结处的电荷转移动力学, 可深入认识结的作用, 进一步指导新材料、新结构的设计合成. 锐钛矿/金红石TiO₂异相结, 可大大提高TiO₂光催化重整生物质制氢的产氢性能. 锐钛矿/金红石异相结处的电荷分离、复合等动力学行为还亟需进一步深入研究, 我们使用时间分辨发光光谱技术, 重点研究了锐钛矿和金红石界面处的电荷转移过程及其对电荷复合过程的影响机制.

我们制备了一系列具有不同晶相组成的TiO₂催化剂, 使用XRD和表面灵敏的紫外拉曼光谱表征确定了样品的表面和体相组成, 研究其光致发光性质并与其晶相组成相关联. 发现, TiO₂的发光行为与其晶相结构直接相关, 特别是与其表面晶相结构存在密切关系. 其中, 500 nm的可见发光带与锐钛矿晶相相关, 而835 nm的近红外发光带与金红石晶相相关. 分析

可见发光带强度随 TiO_2 晶相组成的变化,发现 TiO_2 粒子中存在少量金红石成分时,可见发光带强度不仅未猝灭,反而有一个明显的增强效应,同时,近红外发光峰的出现也存在一定的延后现象. 这些结果表明锐钛矿/金红石异相结处存在金红石向锐钛矿的电荷转移过程.

进一步,使用时间分辨发光光谱研究可见发光带和近红外发光带的衰减动力学,从而分析揭示锐钛矿/金红石相对锐钛矿和金红石的载流子动力学的影响机制. 对于可见发光带来说,锐钛矿/金红石异相结的存在使可见发光带的衰减速率在微秒时间尺度减慢,而在毫秒时间尺度反而衰减变快. 在金红石为主要晶相的混相氧化钛中(如 TiO_2 -800),还观测到了一个新的约 $0.43\ \mu\text{s}$ 的快衰减成分,表明锐钛矿向金红石的载流子转移过程. 对于近红外发光带来说,与可见发光带类似,在微秒时间尺度的衰减也明显变慢,寿命可增长一倍以上,而在毫秒时间尺度的衰减速率没有明显变化. 特别是,在锐钛矿/金红石异相结存在条件下,除长于 $40\ \mu\text{s}$ 的微秒衰减成分外,基本所有混相 TiO_2 样品都显示出 $\sim 2\ \mu\text{s}$ 的快衰减成分,且此快衰减成分的比例受样品晶相组成、制备方法等影响,可达到22%左右. 这一快衰减成分的出现,证明了锐钛矿/金红石异相结处存在金红石向锐钛矿的载流子转移过程.

我们通过发光光谱技术研究了锐钛矿/金红石异相结在电荷分离复合过程中的作用. 研究发现,锐钛矿/金红石相结存在条件下,可见和近红外发光带都出现了一个新的快衰减成分,证明相结处存在快速的电荷分离过程. 由于相结促进电荷分离,在微秒时间尺度抑制了电荷复合,从而使发光衰减明显变慢. 而在毫秒时间尺度,电荷复合速率并没有抑制效果. 因此,我们提出锐钛矿/金红石相结对光催化活性的促进作用,主要是因为微秒时间尺度促进电荷的有效分离,从而使微秒时间尺度存在更大量的光生电荷参与光催化过程.

关键词: 氧化钛; 锐钛矿/金红石相结; 电荷分离; 电荷复合; 时间分辨发光光谱

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