A novel TiO₂ with a large amount of bulk intrinsic defects—Visible-light-responded photocatalytic activity induced by foreign trap

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A novel TiO₂ (anatase) containing a large amount of single electron trapped oxygen vacancies (SETOV) was prepared by dehydration of titanic acid nanotubes. This novel TiO₂ contains high concentration intrinsic defects in bulk structure, while its surface still remains the stoichiometric structure to protect them. And this novel TiO₂ itself has the visible light absorption without any doping, so we call it as the third generation of TiO₂. However, it is regretted that this novel TiO₂ (A) only has photocatalytic activity under UV light irradiation, and was inactive for the visible light. The true reasons for this phenomenon were investigated by the transient IR absorption and photoluminescence spectra. Through constructing the foreign electron traps (PdO, PtO₂), the photocatalytic oxidation of propylene under visible light irradiation was successfully achieved. The removal yield of propylene (C₃H₆) reached 7.6% and 28% on 2 wt.% PtO₂/novel TiO₂ and 2 wt.% PdO/novel TiO₂, respectively. By comparison with the noble metal electron traps (Pt, Pd), we found that the effective foreign electron traps need to satisfy two conditions: (1) its work function should situate in the range of E_g(TiO₂); (2) O₂ adsorbs on it undissociatively. This work opens up a new route for the investigation of solar-energy-available TiO₂.

the third generation of TiO₂, titanic acid nanotubes, electron trap, oxygen vacancy, visible-light-responded photocatalysis

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TiO₂ became the most popular photocatalyst since the discovery of the Fujishima-Honda effect [1]; however, it can only work under UV light. For utilizing more visible light of the solar spectrum, a great deal of work on doping of TiO₂ has been done by many scientists. Doping generated a large amount of non-intrinsic defects within TiO₂ crystal lattice, people called this doped TiO₂ as the second generation of TiO₂ [2]. Two kinds of materials are often doped in TiO₂ to extend the optical absorbance: (1) metal ions, such as Cr, V, Fe, Pb, Cu, etc. [3–6]. They can extend the photo-response of TiO₂ to the visible light region, however, the doped metal ions can also play the role of the recombination centers to reduce its photocatalytic activity [7]; (2) non-

metallic ions, such as C, N, F, P, S, etc. Recently, much attention has been focused on the nitrogen doping [8–13]. It should be emphasized is that the origin of the visible-light-responded photocatalytic activity of N-doped TiO₂ still remains disputable [14–19]. The redox potential of the doped nitrogen (e.g. –NO) exists within V_{cb} to V_{vb} of TiO₂ [20], so the photoelectrochemical stability of the N-doped TiO₂ may be a question for the practical application.

In addition to the non-intrinsic defects can make the photo-response of TiO₂ red-shift, the intrinsic defects can also play the same role. As well known, when TiO₂ was reduced in H₂ atmosphere or treated under vacuum at high temperature, two kinds of intrinsic defects (i.e. oxygen vacancies denoted as $V_o^{\cdot\cdot}$, and Ti^{3+}) would form on TiO₂ surface simultaneously [21–23]. The energy levels of both in-

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intrinsic defects are within E_g (TiO_2). $\text{V}_\text{O}^{\cdot\cdot}$ and Ti^{3+} were easily to react with the ambient oxygen to recover the original surface stoichiometric state of TiO_2 , so they are not stable and cannot be utilized in the practical visible photocatalysis. Then, we wonder how to prepare a TiO_2 with intrinsic defects in bulk and stoichiometric structure on surface. To the best of our knowledge, there have no report about it up to now.

In 1998, Kasuga et al. [24] obtained a nanotube material by treating anatase TiO_2 powders with a 10 mol/L NaOH aqueous solution at 110°C. Following his prepared method, we confirmed the detailed chemical structure of this nanotube material as $\text{Na}_2\text{Ti}_2\text{O}_2(\text{OH})_2$. Nanotube $\text{Na}_2\text{Ti}_2\text{O}_2(\text{OH})_2$ can convert to nanotube titanic acid ($\text{H}_2\text{Ti}_2\text{O}_2(\text{OH})_2$, NTA) in a pH 1 HCl solution, and both of them belong to the orthorhombic crystalline system [25–27]. In our former work [28–31], the formation mechanism, optical property and band structure of the nanotube $\text{Na}_2\text{Ti}_2\text{O}_2(\text{OH})_2$ or $\text{H}_2\text{Ti}_2\text{O}_2(\text{OH})_2$ have been investigated systematically and intensively.

When NTA was dehydrated at an elevated temperature in air, a novel TiO_2 (anatase) was obtained. ESR determination revealed that it contains a large amount of the intrinsic defects: single electron trapped oxygen vacancy (SETOV, denoted as $\text{V}_\text{O}^{\cdot}$) and Ti^{3+} [28–31]. The concentration of $\text{V}_\text{O}^{\cdot}$ obtained from the hydration of NTA at 400°C reached 4.6×10^{24} spin/ m^3 [32]. Through investigating the relationship between the Stokes shift and the excitation wavelength of the visible light, we found that SETOV with high concentration forms a sub-band within E_g (TiO_2). The top and bottom of the sub-band is 2.27 and 1.79 eV higher than the valence band of TiO_2 , and the gap of the sub-band is 0.48 eV [33]. This kind of novel TiO_2 (A) possesses not only a broad optical response from UV to visible light region, but also a very good chemical stability in air. We call it as the third generation of TiO_2 . This kind of TiO_2 is very different with the conventional TiO_2 (first generation) or doped TiO_2 (second generation). The bulk of the third generation of TiO_2 has a large amount of the intrinsic defects, and the surface remains the stoichiometric structure to protect them [34]. However, it is regretted that this novel TiO_2 (A) only has UV photocatalytic activity, and was inactive for the visible light. In this paper, we studied the structure, optical properties and lifetime of the conduction band electrons of the novel TiO_2 (A), and found out the true reason of its inactive photocatalytic activity in visible light. Based on the above study, we adopted some foreign traps on the novel TiO_2 (A) to induce the transfer of the bulk visible-light-generated electrons to its surface, and obtained a visible-light-responded photocatalyst successfully.

1 Experimental

1.1 Preparation of the novel TiO_2 (A) and PtO_2/PdO loaded novel TiO_2 (A)

Nanotube titanic acid ($\text{H}_2\text{Ti}_2\text{O}_4(\text{OH})_2$, NTA) was prepared

using concentrated NaOH and TiO_2 as the raw materials, according to a typical procedure described previously [25,26]. The novel TiO_2 (A) was obtained by treating NTA in air at $T > 400^\circ\text{C}$ for 2–3 h.

The PtO_2/PdO loaded novel TiO_2 (A) was prepared by simple grinding the mixture of PtO_2 (or PdO) and the novel TiO_2 (A). PdO (99.9%) was purchased from Alfa Aesar company. And PtO_2 was presented by Lanzhou Institute of Chemical Physics, CAS. Pd^0 , Pt^0 were the reduced products of PdO , PtO_2 in H_2 flow at 400°C for 4 h. The loaded amount of the cocatalyst was 2 wt.%.

1.2 Characterization

Diffuse reflectance spectra (DRS) were recorded on a Shimadzu U-3010 spectrometer. X-Ray diffraction (XRD) patterns were measured on a Philips X'Pert Pro X-ray diffractometer (Holland) ($\text{Cu K}\alpha$ radiation, 2θ range 5° – 90° , scan step size 0.08° , time per step 1.0 s, generator voltage 40 kV, tube current 40 mA). Photoluminescence (PL) spectra were determined using a SPEX F 212 spectrometer. *In-situ* IR spectra were recorded on a Nicolet 870 FTIR spectrometer with a MCT, the IR cell with the sample was evacuated and dry air was then introduced. X-ray photoelectron spectroscopy (XPS) characterizations were performed using a Shimadzu Axis Ultra multifunctional X-ray photoelectron spectrometer. The energy scale of the spectra was corrected using the binding energy of adventitious carbon $\text{C1s}=284.8$ eV; quantitative analysis of the surface elemental composition was accomplished by a computer program using the XPS sensitivity factors provided by the Shimadzu Co.

1.3 Evaluation of photocatalytic activity

The photocatalytic activity of catalysts was evaluated by monitoring the photocatalytic oxidation reaction of propylene. The 30 ± 1 mg of photocatalyst was dispersed in 10 mL of de-ionized water and spread on the rough surface of a glass plate ($0.9 \text{ cm} \times 11 \text{ cm} \times 0.2 \text{ cm}$). The glass plate was then put into a flat quartz tube reactor with a dead space of 14 mL. A 500 W xenon lamp was used as the visible light source. Between the xenon lamp and reactor were inserted a cutoff filter ($\lambda > 420 \text{ nm}$) and a water cell to eliminate the ultraviolet and infrared light, outputting visible light ($\lambda > 420 \text{ nm}$) with an intensity of about 8.0 mW/cm^2 . A black-light lamp (4 W, main wavelength of 365 nm) was used as the ultraviolet source, and its light intensity was determined to be 2.5 mW/cm^2 . The feed gas was made up of pure C_3H_6 and dry air, in which the ratio of C_3H_6 and air was $600/10^6$ (that is, 600 ppm), and was stored in a high-pressure cylinder. The concentration of C_3H_6 and CO_2 was determined by a chromatographic method (on a Shimadzu GAS CHROMATOGRAPH GC-9A, which was equipped with a GDX-502 column, a Flame ionization detector (FID) and a reactor loaded with Ni catalyst for the methanization of CO_2 , for *in-situ*

analysis). The sensitivity for C_3H_6 analysis was 1 ppm. The C_3H_6 removal (x) = $(C_0 - C)/C_0 \times 100\%$, where C_0 refers to the initial concentration of C_3H_6 .

2 Results and discussion

2.1 Transient IR absorption

The third generation of TiO_2 derived from dehydrate NTA at different elevated temperature ($400^\circ C \leq T \leq 700^\circ C$) showed both UV light and visible light response (Figure 1(a)), and they belonged to the anatase phase structure (Figure 1(b)). However, this kind of novel TiO_2 (A) is only UV active in photocatalytic oxidation of C_3H_6 , and it did not show any activity under visible light (Figure 2). This novel TiO_2 (A) has visible light absorption, but why it has no photocatalytic activity? At one time, we thought that if this phenomenon was possibly resulted from its strong photo-luminescence (PL) under visible light. However, this doubt was denied after the transient IR absorption spectra of both P25- TiO_2 and novel TiO_2 (A) were determined. The transient IR absorption of $1000\text{--}3000\text{ cm}^{-1}$ is a powerful tool for investigating the lifetime of the photo-generated electrons in the conduction band [35–37]. Figure 3 illustrated the transient IR absorption curves of P25 and novel TiO_2 (A) determined at the identical conditions. Using ns pulse of 355 nm laser as the excitation light, the electron concentrations (proportional to absorbance A) obtained in both conduction bands are approximately same, but the decay rates are very different. The time decayed to zero is ca. 0.2 s for P25- TiO_2 , while it is ca. 8.5 s for the novel TiO_2 (A). It indicates that the lifetime of conduction band electrons (τ) of the latter is 43 times longer than that of the former. There are two routes for the decay of photo-generated electrons in conduction band: (1) bulk recombination, (2) transfer to the surface to conduct the chemical reaction. If there were no reactants on the surface, τ would be controlled by the bulk recombination rate (r_{recomb} , $\tau \propto 1/r_{\text{recomb}}$). Bulk recombination can be radiative to emit fluorescence or/and non-radiative to release heat, which only depends on the semiconductor structure and is irrelevant to the activity of photocatalysts. The photocatalytic oxidation results of propylene (Figure 2) illuminated that when the reactants present, though τ of P25- TiO_2 is very shorter, its UV light-generated conduction band electrons can transfer to surface to conduct reactions, but for longer τ of visible light-generated conduction band electrons of novel TiO_2 (A) can't, what is the reason?

2.2 Surface reconstruction and electron trap

In the gas-solid photocatalytic reaction of TiO_2 , the oxidized removal of organic pollutants was realized by using superoxide $O_2^-(a)$ as the oxidant [3–7,36]. The formation of $O_2^-(a)$ was the preliminary step, then through a complex interme-

Figure 1 The UV-vis DRS spectra (a) and XRD spectra (b) of the titanic acid nanotubes and the novel TiO_2 .

Figure 2 The photocatalytic activity of P25- TiO_2 and novel TiO_2 under UV and visible light irradiation.

diolate reactions, the final mineralized products (CO_2 and H_2O) were obtained:

Reaction 1 only takes place when the bulk photo-generated electron was transferred to the surface. The precondition for

Figure 3 Transient IR absorption spectra of P25 and the novel TiO₂.

transfer the bulk electrons out is that there must have electron traps on TiO₂ surface, whose energy level should be lower than the edge of the conduction band of TiO₂.

The stoichiometric TiO₂ surface consists of Ti⁴⁺ and O²⁻ ions. The energy difference between Ti3d LUMO orbital and O2p HOMO orbital equals to 3.2 eV. When the energy of the incident light is larger than 3.2 eV, O2p electron would be excited to Ti3d orbital to form Ti³⁺ and O⁻ ions. According to the Frank-Condon's principle, the change of valence state of surface ions will result in the surface reconstruction to generate new sites with lower energy than that of the conduction band edge [38]. The new sites can play the role of electron traps to accept the photo-generated electrons coming from the conduction band. Figure 4(a) and (b) indicated that a PL peak ($\lambda_{\text{PL}}=470$ nm corresponding to $E_{\text{PL}}=2.6$ eV) appeared when the excitation wavelength (λ_{ex}) was from 360 to 390 nm for both P25-TiO₂ and novel TiO₂ (A). This PL peak belongs to the emission of $e_{\text{surf}}^- - h_{\text{vb}}^+$ recombination, which can only happen under UV irradiation. Its energy potential is lower than that of the conduction band edge of TiO₂. By means of the second harmonic generation, Shultz et al. [39] also evidenced that Ti³⁺ formed on TiO₂ surface under UV irradiation. Therefore it can be con-

cluded that in the course of gas-solid photocatalysis, the UV light irradiated on any one TiO₂ brings out two effects: (1) to excite the valence band electron to conduction band; (2) to provide electron traps on the surface. While the visible light irradiated on novel TiO₂ (A) only gets effect (1): the valence band electron will jump to the conduction band using the sub-band formed by the single-electron-trapped-oxygen-vacancy as the springboard, and the surface reconstruction for producing electron traps does not occur (Figure 4(c)). So, novel TiO₂ (A) showed the visible light response, but no visible-light-responded photocatalytic activity.

2.3 Constructing the foreign electron trap

Under visible light irradiation, the surface of the novel TiO₂ (A) itself cannot reconstruct to form the electron traps. It enlightens us to adopt foreign electron trap to solve the question of transferring the electrons from the conduction band to the surface to conduct the catalytic reaction.

The thermodynamic requisite for foreign trap materials is that their work function must be situated in the range of $E_{\text{g}}(\text{TiO}_2)$. The noble metals (Pt, Pd) and metal oxides (PtO₂, PdO) are often used as the electron traps to improve the separation of the charge carriers. All of their work functions are situated lower than the conduction band of TiO₂ [20,40,41]. Figure 5 shows their XPS spectra. As well known, Pt⁰ and Pd⁰ are often used as the co-catalyst of TiO₂ to improve the activity in many photocatalytic reactions. This was due to that Pt⁰ and Pd⁰ can act as the effective electron traps to increase the photo-excited charge carrier separation of TiO₂. According to this consideration, we think that Pt⁰/novel TiO₂ (A) and Pd⁰/novel TiO₂ (A) should be active under visible light irradiation. However, the actual results were unexpected. As shown in Figure 6, both Pt⁰/novel TiO₂ (A) and Pd⁰/novel TiO₂ (A) did not show any photocatalytic activity for C₃H₆ oxidation.

Selection of the photocatalytic probe reaction should consider the real reaction mechanism. As well known, the dissociative adsorption of O₂ easily takes place on the noble metal (Pt⁰, Pd⁰), even at very low temperature (eq. (3)) [42,43].

Figure 4 (a) PL spectra of P25-TiO₂ ($\lambda_{\text{ex}}=360\text{--}650$ nm); (b) Deconvoluted PL spectra ($\lambda_{\text{ex}}=360\text{--}390$ nm)₂ of novel TiO₂ (A); (c) PL spectra of novel TiO₂ (A) ($\lambda_{\text{ex}}=360\text{--}650$ nm).

Figure 5 The XPS spectra of foreign electron traps of PtO₂ (a), Pt⁰ (b), PdO (c), Pd⁰ (d).

Figure 6 Removal yield of C₃H₆ (a) and CO₂ formation (A =chromatographic peak area) (b) on different photocatalysts under visible light irradiation.

If photo-generated electrons transferred to Pt⁰/Pd⁰ surface, it would be beneficial to O₂ dissociation (O–O bond rupture energy: in O₂, 5.22 eV; in O₂[−], 4.1 eV) [44,45].

O₂[−](a) cannot form on Pt⁰, Pd⁰ (eq. (4)), therefore the C₃H₆ oxidation removal (eq. (2)) certainly does not happen.

However, the dissociated adsorption of O₂ will not take place on PtO₂, and PdO [41,46]. To replace Pt⁰, Pd⁰ with PtO₂, PdO, as expected, the visible photocatalytic activities on both 2 wt.% PtO₂/novel TiO₂ (A) and 2 wt.% PdO/novel TiO₂ (A) were obtained (Figure 6). The removal yield of propylene (C₃H₆) reached 7.6% and 28%, respectively. The effect of the flow rate of the feed gas on the removal yield

of C₃H₆ and CO₂ formation rate are also investigated (Figure 7), where the specific rate constant $k=3.3 \text{ h}^{-1}$. As a comparison experiment, the photocatalytic reaction of propylene on 2% PdO-P25 was conducted. As shown in Figure 6, no photocatalytic activity was found on 2% PdO-P25. These results indicated that the visible-light-excited electrons come from the novel TiO₂, and the PdO and PtO₂ were only acted as the electron traps.

For further improve the photocatalytic activity and push the practical application, preparing the nanostructured PtO₂/PdO loaded novel TiO₂ (A) and attempting other cheap and efficient foreign-trap material is under investigation.

3 Conclusions

In summary, we obtained the following conclusions: (1) A

Figure 7 Visible-light photocatalytic activity of 2 wt.% PdO/Novel TiO₂. (a) Dependence of C₃H₆ conversion on feed gas rate; (b) dependence of CO₂ formation on feed gas flow rate; (c) the specific rate constants.

novel TiO₂ (A) derived from the dehydrate NTA showed the visible light response, but no photocatalytic activity for C₃H₆ oxidation. The reason was possibly that the sub-band of the novel TiO₂ (A) plays the role of mediator for the transition of valence band electron to the conduction band under visible light irradiation, while the surface reconstruction for producing electron traps does not happen. The bulk photo-generated electrons cannot be transferred to the surface, so the photocatalytic reaction cannot proceed. (2) The visible photocatalytic oxidation of C₃H₆ was successively realized by adding foreign electron traps (PtO₂, PdO) on the novel TiO₂ (A). The removal yield of C₃H₆ on PtO₂/novel TiO₂ (A) and PdO/novel TiO₂ (A) reached 7.6% and 28%, respectively. At the same time, a number of mineralization products (CO₂) were obtained. The prerequisite for the effective foreign electron traps need to satisfy two conditions: its work function situated in the range of *E_g*(TiO₂) and O₂ adsorbed on it undissociatively. (3) The finding of the reason that the novel TiO₂ (A) having the visible light response but no photocatalytic activity opens up a new route for the investigation of solar-energy-available TiO₂. The novel TiO₂ (A) with high concentration of intrinsic defects in bulk and stoichiometry on surface was called the third generation of TiO₂.

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