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Article

Highly photostable palladium-loaded TiO₂ nanotubes and the active species in the photodegradation of methyl orange

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ABSTRACT

Highly photostable palladium-loaded TiO₂ nanotubes (Pd/TNTs) were prepared by a simple photo-decomposition method and characterized by inductively coupled plasma, X-ray diffraction, UV-visible light diffuse reflectance spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy, N₂ adsorption-desorption, and photocurrent measurement. TEM images showed that the samples had a tubular structure. XPS results revealed that most of the palladium was present as Pd⁰. The photocatalytic performance was evaluated by monitoring the catalytic activity for the degradation of methyl orange solution under both UV and simulated sunlight irradiation. Pd/TNTs with 0.3 wt% Pd displayed higher activity than P25. The active species in the photocatalytic process were investigated by using different types of active species scavengers. h_ν⁺ was the major reactive species in the photodegradation over the Pd/TNTs.

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1. Introduction

Due to the non-toxicity and photostability, TiO₂-based nanomaterials are widely used as the semiconductor photocatalyst for water splitting and water and air purification [1–5]. However, the photocatalytic activity of TiO₂ is limited by its intrinsic defects. On the one hand, TiO₂ can be excited only by UV light, which is a small fraction of the solar spectrum. On the other hand, the high recombination rate of the photogenerated electron-hole pairs significantly reduces the photocatalytic efficiency. To overcome these drawbacks, many methods, such as the use of binary oxides, transition metal and nonmetal doping,

dye sensitization, and supporting TiO₂ on activated carbon, carbon nanotubes, graphite, and polymeric graphitic carbon nitride, have been used to reduce the recombination rate of photogenerated electron-hole pairs or shift the optical response of TiO₂ to the visible light region [6–12].

In recent years, one dimensional TiO₂ nanostructure materials, including nanorods, nanowires, nanofibers, nanobelts, and nanotubes, have attracted great interest for their peculiar architecture, high mass transport rate, and remarkable light harvest property [13–15]. Among these materials, TiO₂ nanotubes (TNTs) have been widely seen as an optimal nanostructure for enhancing photocatalytic activity. In 1998, Kasuga et al.

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[16] developed a simple hydrothermal method to convert TiO_2 particles into nanotubes. Since then, the practical application of TNTs has been extensively investigated. It is well known that titanate nanotubes made via a hydrothermal treatment are formed by the scrolling of TiO_2 sheets and there are many coordinative unsaturated O atoms and OH groups on the inner and outer surfaces of the nanotubes. To keep the structure of the nanotube intact under irradiation, the amount of OH groups and unsaturated O atoms, which may induce the collapse of the nanotubes during calcination and irradiation, must be decreased [17,18]. In our previous work, we reported the photocatalytic degradation of methyl orange under UV irradiation over Pd-loaded TiO_2 nanofibers, which were prepared from PdCl_2 and hydrogen titanate nanotubes by a photodecomposition method [19]. The photocatalytic activity of TiO_2 was enhanced after palladium loading, but the nanotubular structure was destroyed in the process of irradiation, which was detrimental for the photocatalytic activity. Hence, it is essential to explore the preparation of TNTs with high photostability and photocatalytic activity.

In order to induce the response of the semiconductor to visible light, the deposition of noble metals on the semiconductor has been investigated. In particular, Pd loaded on semiconductors exhibits remarkable performance in photocatalytic reactions [20–23]. It is well known that Pd nanoparticles loaded on a semiconductor are used as an electron reservoir to prolong the lifetime of the electron-hole pairs photogenerated by the semiconductor, thereby enhancing the photocatalytic efficiency.

In this work, thermally stable TNTs were used as the support, and Pd nanoparticles were loaded on the TNTs by photodeposition to synthesis Pd/TNTs with high photostability and photocatalytic activity. The samples were characterized by X-ray diffraction (XRD), UV-Vis light diffuse reflection spectroscopy (DRS), transmission electron microscopy (TEM), X-ray photoelectron microscopy (XPS), and N_2 physisorption. In addition, the separation and transport efficiency of the photogenerated electron-hole pairs under UV irradiation were studied by photoluminescence (PL) spectroscopy measurements and photoelectrochemistry experiments. The photocatalytic activity was evaluated by the degradation of methyl orange (MO) under both UV and simulated sunlight irradiation conditions. The active species generated in the process of photodegradation were investigated by free radical and hole scavenging experiments.

2. Experimental

2.1. Synthesis of Pd/TNTs

All reagents were analytical grade and used without further purification.

TNTs were synthesized by the hydrothermal treatment reported in a previous report [16]. Pd/TNTs prepared according to the literature [19] were marked as Pd/TNTsA. TNTs and Pd/TNTs prepared according to the approaches reported previously [24] were marked as TNTsB and Pd/TNTsB, respectively.

tively.

Pd/TNTs were synthesized by a photodeposition method. In a typical synthesis, 0.5 g TNTs were dispersed in 20 mL aqueous $\text{Pd}(\text{AC})_2$ solution (10 mL H_2O + 10 mL HAC), and the system was vigorously agitated for 12 h. After low energy sonication for 1 h, the mixture was centrifuged. In order to remove $\text{Pd}(\text{AC})_2$ solution adsorbed on the surface of the TNTs, the TNTs were washed with distilled water. Then the TNTs were transferred into a quartz tube with 30 mL distilled water. The suspension was irradiated for 4 h by a 300 W high pressure mercury lamp under stirring at ambient temperature. The Pd/TNTsA-X and Pd/TNTsB-X (X refers to the Pd mass percentage) obtained were washed with distilled water and ethanol, and then dried at 40 °C in vacuum.

2.2. Characterization

The morphology and microstructure of the catalysts were analyzed by TEM (Philips T20ST). The chemical state of the elements in the catalysts was determined by XPS (Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectrometer), and all binding energy (BE) was calibrated using C 1s (BE = 284.6 eV) as reference. The phase structure of the catalysts was characterized by XRD (Rigaku D/Max-2500 X-ray diffractometer with Cu K_α radiation). The bulk composition of the samples was measured by inductively coupled plasma (ICP-9000, USA Thermo Jarrell-Ash Corp). The optical response of the samples was characterized by UV-Vis DRS (UV3600 UV/Vis spectrometer). The specific surface area of the catalysts was measured at liquid N_2 temperature by the BET method (BET, JW-K). PL data were recorded on an Edinburgh FLS920P spectrophotometer, and the excitation wavelength was 380 nm.

2.3. Photocatalytic activity test

A photoreactor (XPA-7 series) was used to test the photocatalytic activity of the samples. In a typical photodegradation procedure, 0.05 g photocatalyst and 60 mL methyl orange solution (20 mg/L) were put in a quartz tube, which was irradiated with a 300 W high pressure mercury lamp or a 500 W Xe lamp under continuously stirring. At regular time intervals of irradiation, 5 mL of the liquid mixture was withdrawn and centrifuged, and the concentration of methyl orange in the clear solution was measured using a 752/752N UV-Vis spectrometer (Shanghai Sunny Hengping, China) at 463.8 nm, where methyl orange showed its maximum absorption. The results were corrected for the decomposition of methyl orange in the absence of catalyst and its adsorption on the catalyst.

2.4. Photocurrent (PC) measurement

The working electrode was prepared on a rectangle Ti foil (size 8 mm × 8 mm, thickness 0.127 mm, purity > 99.7%, Sigma-Aldrich), which was treated by sonication in acetone, alcohol, and water in sequence for 30 min before use. The cleaned Ti foil was chemically etched with a mixture of HF, HNO_3 , and H_2O ($V_{\text{HF}}:V_{\text{HNO}_3}:V_{\text{H}_2\text{O}} = 1:4:5$) for 30 s followed by rinsing with

distilled water, and then kept in alcohol. The catalyst powder (5 mg) and alcohol (1 mL) were sonicated for 30 min to get a slurry. The slurry was spin-coated on the Ti foil at an initial spin rate of 500 rpm for 9 s and then 2000 rpm for 10 s. After air drying, the prepared working electrode was heated at 100 °C for 6 h in air to enhance the contact between the Ti foil and catalyst. Photocurrent measurement was carried out using a conventional three electrode setup connected to an electrochemical station (CHI 604D, Shanghai Chenhua, China). In this electrochemical system, the catalyst/Ti foil was used as the working electrode. A Pt wire was used as the counter electrode, and an Ag/AgCl electrode (saturated KCl) was used as the reference electrode. The electrolyte was phosphate buffered saline (PBS) solution (0.01 mol/L). A 365 nm LED served as the light source. The measurement was carried out at a constant potential of +0.5 V versus the working electrode.

3. Results and discussion

3.1. XRD and DRS results

Fig. 1 shows the XRD patterns of TNTsB, as-synthesized Pd/TNTsB-*X* (*X* = 0.1, 0.2, 0.3, and 0.4), and Pd/TNTsA-0.3. The diffraction peaks of anatase TiO₂ (JCPDS21-1272) were easily detected in all the XRD patterns. The peaks at 25.43°, 37.92°, 48.03°, 53.97°, 55.05°, 62.70°, 68.80°, 70.39°, and 75.05° were the diffractions of the (101), (004), (200), (105), (211), (204), (116), (200), and (215) crystal planes of TiO₂, respectively. No obvious titanate peak was observed with Pd/TNTsA. It has been reported that hydrogen titanate can be converted into anatase TiO₂ by the illumination process [19]. No peak related to Pd was observed in Fig. 1(2)–(6). This can be attributed to the high dispersion of Pd and the low Pd content.

The optical absorption property of the samples was characterized by UV-Vis DRS measurement. Fig. 2 depicts the absorption spectra of TNTsB, as-synthesized Pd/TNTsA-0.3, and Pd/TNTsB-0.3. Because they are an indirect band gap semiconductor, the band gap energy of TNTsB and Pd/TNTs was estimated from a plot of the transformed Kubelka-Munk func-

Fig. 1. XRD patterns of TNTsB (1), Pd/TNTsB-*X* (*X* = 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5)), and Pd/TNTsA-0.3 (6).

Fig. 2. UV-Vis DRS absorption spectra of TNTsB (1), Pd/TNTsA-0.3 (2), and Pd/TNTsB-0.3 (3).

tion versus the energy of the exciting light. The band gap energy of TNTsB, Pd/TNTsA-0.3, and Pd/TNTsB-0.3 estimated from Fig. 2 were 3.23, 3.09, and 3.03 eV, respectively. By comparing the three curves, Pd/TNTsB-0.3 was shown to have the highest absorbance intensity, and the absorption edge showed a small red shift. Hence, Pd/TNTs would have visible light photocatalysis. Similar results have been reported in the literature for the Pd-TiO₂ system [25,26].

3.2. TEM and XPS results

Fig. 3 shows the TEM and HR-TEM images and EDX spectra of Pd/TNTsA-0.3 and Pd/TNTsB-0.3. As can be seen clearly in Fig. 3(a), the nanotube of Pd/TNTsA-0.3 was short in length, and most nanotubes were broken and agglomerated, indicating the collapse of the tubular structure. Compared to Fig. 3(a),

Fig. 3. TEM images of Pd/TNTsA-0.3 (a) and Pd/TNTsB-0.3 (b); HR-TEM image (c) and EDX spectrum (d) of Pd/TNTsB-0.3.

Pd/TNTsB-0.3 (Fig. 3(b)) showed an obvious nanotube morphology. Each individual nanotube was hundreds of nm in length, and no collapse occurred in the photodeposition process. Hence, we have prepared Pd/TNTsB with high photostability. The reasonable interpretation is that the liquid sol existing in the interlayer spacing of the TNTsB decomposed into many small TiO_2 nanoparticles during the calcination, which increased the thickness of the wall of the nanotubes and they linked with the unsaturated O groups on the nanotubes [27]. At high magnification (Fig. 3(c)), Pd/TNTsB-0.3 was seen to have a multiwall tubular structure, and the interlayer spacing was 0.7 nm. Some black particles deposited on the outer and inner surface of the nanotubes can be detected. These would be Pd nanoparticles. The formation of Pd nanoparticles would be as follows. TiO_2 absorbed UV light, and electron-hole pairs were generated. Pd^{2+} ions captured the electrons from the excited TiO_2 and were reduced to metallic Pd. EDX analysis (Fig. 3(d)) showed that Ti and O were the main components, and a weak peak of Pd was also observed. This confirmed the formation of Pd/TNTsB.

To investigate the chemical state of the Pd nanoparticles, XPS analysis was carried out. Fig. 4 shows the Pd 3d XPS spectra. The Pd 3d_{5/2} peak consisted of two components at 335.9 eV and 337.0 eV, which were attributed to metallic Pd and PdO, respectively [28]. Most of the Pd on the surface of the catalyst were present as Pd⁰.

3.3. Photoluminescence measurement and photoelectrochemical experiments

Photoluminescence (PL) spectra have been used to study the transfer of the photogenerated electron-hole pairs. Generally, a higher PL intensity indicates a higher recombination rate of photogenerated electron-hole pairs, and a lower PL intensity expresses a lower recombination rate of photogenerated electron-hole pairs [29,30]. To investigate the photoelectric properties, the PL spectra of the samples excited at 380 nm at room temperature are shown in Fig. 5. The PL bands of TNTsB can be fitted with three Gaussian peaks with maximum at 427, 525, and 630 nm. The peak at 427 nm was attributed to self-trapped excitons localized on TiO_6 octahedra. The other two PL emission peaks at 525 and 630 nm were assigned to oxygen vacan-

Fig. 4. Pd 3d XPS spectra of Pd/TNTsB-0.3.

cies existing on the surface and within the TiO_2 , respectively [31,32]. The PL intensity decreased in the order TNTsB > Pd/TNTsA-0.3 > Pd/TNTsB-0.3, which means that Pd acted as a trapping site, capturing photogenerated electrons from the conduction band and effectively inhibiting the recombination of photogenerated electron-hole pairs. Thus Pd/TNTsB-0.3 would exhibit a higher photocatalytic activity than Pd/TNTsA-0.3 and TNTsB.

In order to investigate the separation efficiency of the photogenerated electron-hole pairs in the original TNTs and Pd/TNTs, the transient photocurrent response was measured by several on-off cycles of illumination. The results are displayed in Fig. 6. A sharply increased photocurrent response appeared for all the working electrodes when a pulse of 365 nm LED irradiation was applied. The photocurrents generated were reproducible and stable during four on-off intermittent irradiation cycles. Both tested Pd/TNTs/Ti electrodes presented a higher photocurrent response than the original TNTs/Ti electrode under the same conditions, which showed that the modification with Pd nanoparticles efficiently separated photogenerated electron-hole pairs. Moreover, the transient photocurrent density of Pd/TNTsB-0.3/Ti was higher than that of Pd/TNTsA-0.3/Ti under irradiation. This would be due to that the tubular Pd/TNTsB has a higher SSA area and Pd dispersion than Pd/TNTsA.

Fig. 5. Room temperature PL spectra of TNTsB (1), Pd/TNTsA-0.3 (2), and Pd/TNTsB-0.3 (3) under the excitation wavelength of 380 nm (a); fitted Gaussian peaks for TNTsB (b).

Fig. 6. Photocurrent responses of TNTsB (a), Pd/TNTsA-0.3 (b), and Pd/TNTsB-0.3 (c) electrodes in phosphate buffered saline (PBS) electrolyte solution (0.01 mol/L) under 365 nm LED irradiation. The working electrode potential was constant at +0.5 V.

3.4. Photocatalytic activity

The photocatalytic activity of the samples was evaluated by the photodegradation of MO in water under UV or simulated sunlight irradiation. Fig. 7 shows the photocatalytic activity of the samples under UV or simulated sunlight irradiation and the curves of $\ln(C_0/C)$ versus irradiation time. Obviously, the photocatalytic activity of the TNTs was significantly enhanced after the loading of Pd on the TiO_2 nanotubes. The activity of Pd/TNTsB with different Pd loadings increased with Pd content from 0.1 wt% to 0.3 wt% and then decreased when the Pd loading was further increased to 0.4 wt%. The optimum Pd loading for achieving the highest activity was 0.3 wt% under both UV and simulated sunlight irradiation. In addition, from the inset in Fig. 7, it can be seen that the photocatalytic degradation obeyed first order kinetics, $\ln(C_0/C) = kt$. Table 1 shows the k values of the samples. From Table 1, it can be seen that the k value of Pd/TNTsB-0.3 was the largest. It is noteworthy that the photocatalytic activity of Pd/TNTsB-0.3 was higher than P25.

Table 1
Rate constant over the samples for MO degradation under UV (k/min^{-1}) and simulated sunlight irradiation (k/h^{-1}).

Sample	k/min^{-1}	k/h^{-1}
TNTsB	0.06	0.23
Pd/TNTsB-0.1	0.11	0.41
Pd/TNTsB-0.2	0.16	0.52
Pd/TNTsB-0.3	0.25	0.62
Pd/TNTsB-0.4	0.18	0.54
Pd/TNTsA-0.3	0.17	0.52
P25	0.19	0.54

As discussed above, most of the Pd was present as Pd^0 . The photocatalytic reaction rate of TiO_2 was not high owing to the quick recombination of the charge carriers. After Pd was loaded on the TiO_2 nanotubes, Pd accelerated the interfacial electron transfer process and changed the excitation energy of the TiO_2 semiconductor. The formation of a Schottky barrier between Pd and TiO_2 allowed the photogenerated electrons to be captured by Pd easily, and then the lifetime of the electron-hole pairs was prolonged [25,33]. As a result, enhanced photocatalytic activity was exhibited. The increase in photocatalytic activity of Pd/TNTsB with Pd loading showed that there was an optimum Pd loading (0.3 wt% in this work), at which there was the most efficient separation of the photogenerated hole-electron pairs. A further increase in Pd content reduced the photocatalytic activity. The catalysts with too high a Pd loading may have new defect sites, which will induce the recombination of photogenerated electron-hole pairs.

To compare the photocatalytic performance of Pd/TNTsA and Pd/TNTsB, the photocatalytic curve of Pd/TNTsA-0.3 is also displayed in Fig. 7. The k value is listed in Table 1. Pd/TNTsB-0.3 showed a higher photocatalytic activity and larger k value than Pd/TNTsA-0.3. The difference in the photocatalytic degradation of MO over Pd/TNTsA-0.3 and Pd/TNTsB-0.3 under both UV and simulated sunlight irradiation was mainly due to the specific areas of the catalysts. The BET specific surface areas of Pd/TNTsA-0.3 and Pd/TNTsB-0.3 were 184.3 and 268.9 m^2/g , respectively. As discussed with the

Fig. 7. Photocatalytic activity of TNTsB (1), Pd/TNTsB-0.1 (2), Pd/TNTsB-0.2 (3), Pd/TNTsB-0.3 (4), Pd/TNTsB-0.4 (5), Pd/TNTsA-0.3 (6), and P25 (7) under UV (a) and simulated sunlight irradiation (b) (the insets are the plots of $\ln(C_0/C)$ vs irradiation time).

Fig. 8. Influence of various scavengers on the photocatalytic activity of Pd/TNTsB-0.1 for the degradation of MO under UV (a) and simulated sunlight irradiation (b). KI: potassium iodine; AO: ammonium oxalate; TBA: *tert*-butyl alcohol.

TEM result, the tubular structure of Pd/TNTsA was broken, whereas the tubular structure of Pd/TNTsB was maintained under the same conditions. The collapse of the nanotubes resulted in the decrease of the surface area. On a larger surface, the active species are better dispersed.

3.5. Free radical and hole scavenging experiments

According to the photocatalytic mechanism [34,35], the photogenerated electrons can be scavenged by oxygen to form $O_2^{\cdot-}/HO_2^{\cdot}$ radicals and H_2O_2 . On the other hand, the photogenerated holes can be partially captured by OH^- or H_2O to form $\cdot OH$ radicals. Thus various reactive species, such as h_{vb}^+ , $\cdot OH$, $O_2^{\cdot-}/HO_2^{\cdot}$ as well as H_2O_2 , exist during the photocatalytic degradation of organics. To determine the main reactive species during the photocatalytic degradation of MO under irradiation, different scavengers were used to remove the reactive species. In this work, *tert*-butyl alcohol (TBA) was utilized for scavenging $\cdot OH$ radicals in solution, potassium iodine (KI) was used as the scavenger of both $\cdot OH$ radicals and h_{vb}^+ , ammonium oxalate (AO) was selected as the hole scavenger, and $Cr(VI)$ was used as an electron scavenger under bubbling nitrogen condition [28,36–38].

Fig. 8(a) presents the influence of various scavengers on the photocatalytic activity of Pd/TNTsB-0.1. Without scavengers, the photocatalytic degradation of MO was 100% after UV irradiation for 20 min, which can be attributed to the contributions of all reactive species. Compared to the scavenger-free Pd/TNTsB photocatalytic system, the photodegradation of MO was almost completely inhibited after the addition of KI (0.05 mmol) to the reaction system, which scavenged the h_{vb}^+ and $\cdot OH$ active species, demonstrating that both h_{vb}^+ and $\cdot OH$ species were mainly responsible for the degradation of MO. Furthermore, in order to distinguish the contribution of $\cdot OH$ radicals from h_{vb}^+ , 0.05 mmol TBA and 0.05 mmol AO were added into the reaction system. After AO was added, the degradation rate of MO was remarkably decreased. However, after TBA was added, the degradation rate was only slightly decreased. $K_2Cr_2O_7$ can exclude the formation of H_2O_2 and $O_2^{\cdot-}/HO_2^{\cdot}$ in the

case of bubbling nitrogen, and the photocatalytic degradation of MO was moderately decreased after the addition of $K_2Cr_2O_7$. To summarize, it was concluded that the photodegradation of MO over Pd/TNTs under UV irradiation was driven by the participation of h_{vb}^+ , and to a moderate extent by $O_2^{\cdot-}/HO_2^{\cdot}$ and H_2O_2 . Fig. 8(b) displays the influence of the various scavengers on the photocatalytic activity of Pd/TNTsB-0.1 under simulated sunlight irradiation. This showed that h_{vb}^+ was also the main reactive species because the degradation of MO was decreased significantly in the presence of AO. However, different from the photocatalytic system irradiated with UV, the photodegradation rate of MO was only slightly suppressed after the addition of 0.05 mmol $K_2Cr_2O_7$ under bubbling nitrogen condition. This indicates that the contribution of e_{cb}^- was limited under simulated sunlight irradiation.

On the basis of the above discussion, it can be stated that h_{vb}^+ was the major reactive species in the photodegradation of MO over Pd/TNTs. The mechanism of the photocatalytic degradation of MO over the heterostructured Pd/TNTs is illustrated in Fig. 9. Under UV radiation, photons excite electrons from the VB of TiO_2 to the CB, forming photo-generated electron

Fig. 9. Mechanism of photocatalytic degradation of MO over Pd/TNTs.

(e_{cb}^-) and holes (h_{vb}^+) pairs. The e_{cb}^- and h_{vb}^+ can recombine quickly, and only a fraction of the e_{cb}^- and holes participate in the photocatalytic reaction, resulting in low activity. The enhanced photocatalytic activity of Pd/TNTs can be ascribed to the Schottky barrier effect that gave a higher potential gradient. The Schottky barrier produced at the metal-semiconductor interface served as an efficient electron trap, thereby retarding photo-generated electron-hole recombination [39,40]. In the presence of Pd, the e_{cb}^- in CB is transferred to Pd nanoparticles rapidly, and the h_{vb}^+ stays in the VB of the TNTs. Subsequently, the e_{cb}^- on the Pd nanoparticles reacts with O_2 to produce $O_2^{\cdot-}/HO_2^{\cdot}$ radicals and H_2O_2 . The oxidative species including h_{vb}^+ , $O_2^{\cdot-}/HO_2^{\cdot}$ radical, and H_2O_2 are responsible for the degradation of MO.

4. Conclusions

Pd/TNTsB photocatalysts with high photostability and photocatalytic activity were synthesized by the photodecomposition method. TEM images showed that the tubular structure of Pd/TNTsB was intact after the photodeposition. Compared to Pd/TNTsA, the intact nanotube structure and larger surface area gave Pd/TNTsB a higher photocatalytic activity. XPS results revealed that most of the Pd were present as Pd^0 , which acted as electron traps and facilitated the separation of photogenerated electron-hole pairs. Pd/TNTsB has a higher photocatalytic activity for the degradation of MO under both UV and simulated sunlight irradiation. When the Pd content was 0.3 wt%, the Pd/TNTsB catalyst showed the highest photocatalytic activity, which was higher than that of P25. The h_{vb}^+ reactive species was demonstrated to be the major reactive species in the photodegradation process of MO over Pd/TNTs.

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Graphical Abstract

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Highly photostable palladium-loaded TiO_2 nanotubes and the active species in the photodegradation of methyl orange

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Highly photostable palladium-loaded TiO_2 nanotubes were prepared by a photodecomposition method. h_{vb}^+ was the major reactive species in the photodegradation of methyl orange (MO) over these Pd/TNTs.

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光稳定二氧化钛纳米管负载钯催化剂光降解甲基橙过程中的活性物种

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摘要: 采用光沉积法制备了光稳定二氧化钛纳米管负载钯催化剂。通过X射线衍射、紫外-可见漫反射光谱、透射电子显微镜(TEM)、氮气吸附-脱附、X射线光电子能谱(XPS)、光致发光光谱和光电流等表征手段研究了催化剂的结构和性质。TEM表明二氧化钛纳米管经光照后仍然保持良好的管状结构; XPS结果表明大部分Pd以零价形式存在。以甲基橙溶液作为模拟废液研究了催化剂在紫外光及模拟日光条件下的光催化活性。当Pd的负载量为0.3 wt%时, 催化剂的光催化活性最高并且优于P25的光催化活性。另外, 通过在光降解过程中加入不同的捕获剂研究了不同氧化活性组分的作用。结果表明, 光生空穴(h_{ν}^{+})在光催化降解过程中起主要作用。

关键词: 二氧化钛纳米管; 钯; 活性物种; 光降解; 甲基橙

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