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Article

Preparation and photocatalytic activity of rutile TiO₂ and goethite composite photocatalysts

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ABSTRACT

Rutile TiO₂ and goethite (α -FeOOH) composite photocatalysts were fabricated by hydrolysis and precipitation using titanium tetrachloride as a precursor and α -FeOOH as a support. The samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy. The results show that at lower temperature, rutile TiO₂ particles coat on the surface of α -FeOOH particles to form rutile TiO₂- α -FeOOH composite photocatalyst. At higher temperature, iron ions are doped into the rutile TiO₂ lattice to form iron-doped rutile TiO₂ tubes; at medium temperature, the sample is a mixture with both composite and iron-doped structures. The photocatalytic activity of the samples is estimated by their ability to degrade methyl orange under irradiation with ultraviolet-visible light (200–800 nm) at ambient temperature. The photocatalytic activities of the samples are improved compared with that of pure rutile TiO₂ and α -FeOOH. The sample containing a mixture of composite and iron-doped structures shows the highest photocatalytic activity of that investigated. As a result, the photocatalytic activity of TiO₂ could be improved effectively by combining with α -FeOOH or doping iron.

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1. Introduction

How to solve environmental issues is currently an important subject. During the next two decades, control of environmental pollution will become a global problem that urgently needs to be solved [1–3]. Use of semiconductor photocatalysts to treat environmental pollution is a promising solution to this problem [4–6]. Many semiconductor photocatalyst materials have been used for this purpose; among them, titanium dioxide (TiO₂) has received intense attention. It has been widely used to treat environmental pollution in water and air [7,8] owing to

its non-toxic and exhibits high photochemical stability, high catalytic efficiency, and strong oxidative ability without secondary pollution.

However, TiO₂ semiconductor photocatalysts possess some obvious disadvantages. First, the band gap of TiO₂ is wide (that of anatase is up to 3.2 eV), corresponding to an absorption threshold of 387.5 nm. This means it only absorbs ultraviolet (UV) light, so it has almost no response to visible light, and can only use approximately 3%–5% of sunlight. Second, the lifetime of photoinduced charge carriers in TiO₂ is very short, ranging from nanoseconds to picoseconds, and their recombination

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rate is high. These shortcomings limit the photocatalytic efficiency of TiO_2 . Therefore, how to improve the photocatalytic efficiency of TiO_2 photocatalysts are important to realize its practical application.

The band gap of TiO_2 photocatalyst can be narrowed and its recombination rate of photoinduced charge carriers can be reduced by controlling its crystal structure and surface physicochemical properties [9]. Such control can be achieved by doping TiO_2 with transition metal ions [10–12] such as Fe^{3+} , Cr^{3+} , Mn^{2+} , and Co^{2+} with full or half-full electronic configuration or non-metallic elements such as N, S, F, and V [13–15], or by combining TiO_2 with a semiconductor with a narrow band gap. In recent years, multiphase composite systems including $\text{Fe}_2\text{O}_3/\text{TiO}_2$ [16], $\text{TiO}_2/\text{SiO}_2$ [17], TiO_2/WO_3 [18], and TiO_2/ZnO [19] have been widely investigated. The semiconductor material $\alpha\text{-FeOOH}$ is used as a support for TiO_2 because of its narrow band gap (2.6 eV). Combining TiO_2 with $\alpha\text{-FeOOH}$ can reduce its band gap and extend its light response to the visible range [20,21]. In addition, $\alpha\text{-FeOOH}$ can provide Fe^{3+} for metal ion doping, and improve the performance of TiO_2 photocatalysts.

$\text{TiO}_2/\alpha\text{-FeOOH}$ composite photocatalysts have been investigated extensively. Liang et al. [20] fabricated a $\text{TiO}_2/\text{FeOOH}$ composite photocatalyst with core-shell structure by hydrolysis and precipitation and noted an obvious synergistic effect between titania and $\alpha\text{-FeOOH}$. In addition, its ability to photocatalytically degrade organic compounds was improved. Rawal et al. [21] found that a $\text{TiO}_2/\text{FeOOH}$ nanocomposite material degraded gaseous 2-propanol into CO_2 under irradiation with visible light ($\lambda \geq 420$ nm), and its degradation efficiency was higher than that of TiO_2 alone. However, current reports rarely consider the relationships between preparation conditions, microstructure and performance of $\text{TiO}_2/\alpha\text{-FeOOH}$ photocatalysts. Here, we report a novel approach to fabricate composite and doped $\text{TiO}_2/\alpha\text{-FeOOH}$ photocatalysts. The effect of preparation conditions on photocatalytically degrade methyl orange is investigated. In addition, the correlation between the photocatalytic performance of the photocatalyst and its microstructure is assessed.

2. Experimental

2.1. Photocatalyst preparation

Rutile $\text{TiO}_2/\alpha\text{-FeOOH}$ photocatalysts was obtained using TiCl_4 as a precursor. Firstly TiCl_4 (Shanghai Meixin Chemical Co., Ltd, China) was added dropwise into deionized water at -10 to 0 °C in an ice-water bath, with a volume ratio of 1:2 of TiCl_4 to deionized water. The mixture was vigorous stirred for 2 h until it changed into a light yellow-green sol, it was aged at room temperature for 10 to 14 h, and TiCl_4 hydrosol [22] was formed.

Then the TiCl_4 hydrosol was diluted by dropping appropriate amount of deionized water under stirring. And a certain mass of $\alpha\text{-FeOOH}$ (Deqing Huayuan Pigment Co., Ltd., China) was dispersed into the above sol according to a molar ratio of Fe to Ti of 1:1. The mixture was divided into five equal parts, each was stirred for 2 h at 30, 45, 60, 75, or 90 °C. The precipi-

tate was filtered, washed with distilled water several times to remove chlorine ions. All the samples were dried in an oven for 12 h at 80 °C, named TY-30-2, TY-45-2, TY-60-2, TY-75-2, and TY-90-2, respectively according to the preparing temperature.

2.2. Photocatalyst characterization

The crystal phase, morphology, microstructure, chemical composition, and valence state of the chemical components in the photocatalysts were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron spectroscopy (XPS), respectively. XRD was performed with a diffractometer (X'Pert PRO Thermo, PANalytical, Holland) using a $\text{Cu } K_\alpha$ radiation source ($\lambda = 0.1541$ nm) under a voltage of 40 kV and current of 40 mA. XRD patterns were recorded with a step size of 0.03° from 15° to 85° . TEM was performed with a high-resolution transmission electron microscope (Tecnai G2 F30 S-Twin, Philips-FEI, Netherlands) at a voltage of 300 kV. XPS was operated on a photoelectron spectrometer (Kratos AXIS Ultra DLD, Shimadzu, Japan).

2.3. Photocatalytic performance test

The performance of photocatalyst's absorb towards light was performed under UV-Vis light. Pure rutile TiO_2 , $\alpha\text{-FeOOH}$, and samples were dispersed respectively to a solution of ethanol and deionized water with a volume ratio of 3:7, translucent solution with a concentration of 10^{-5} g/ml was gained. The mixture was mixed by ultrasound for 5 min, and then separated by centrifugation. The supernatant was analyzed with a UV-Vis spectrophotometer (Shimadzu UV1800, Japan) in the 200–800 nm region.

The photocatalytic performance test was carried out in a custom-made apparatus at room temperature using tungsten and deuterium lamps (wavelength 200–800 nm) as light sources. Taking $\alpha\text{-FeOOH}$ (0.005 g), pure rutile TiO_2 (0.005 g), and samples (0.005 g) added to a methyl orange solution with an initial concentration of 20 mg/L respectively in the dark. The mixture was stirred by ultrasound for 5 min to achieve adsorption equilibrium, and then it was irradiated with UV-vis light to commence photocatalytic degradation. Samples were taken from the reaction solution after different periods (0, 30, 60, 90, 120, 150 and 180 min). The amount of methyl orange remaining in the supernatant obtained after high speed centrifugation for 5 min was analyzed by UV-vis spectroscopy at 462 nm.

3. Results and discussion

3.1. XRD analysis

Figure 1 shows XRD patterns of different samples. The intensity of the diffraction peak of rutile TiO_2 at $2\theta = 27.42^\circ$ (PDF 21-1276) increases as the preparation temperature rise. In contrast, that of $\alpha\text{-FeOOH}$ (PDF 29-0713) decreases gradually

Fig. 1. XRD patterns of α -FeOOH (1), TY-30-2 (2), TY-45-2 (3), TY-60-2 (4), TY-75-2 (5), TY-90-2 (6), prepared at 30, 45, 60, 75, and 90 °C, respectively.

as the preparation temperature increases. At 75 °C or higher, the diffraction peaks of α -FeOOH almost disappear; in particular, the peak at 21.224° disappears completely; only the diffraction peaks of rutile TiO_2 are observed. This indicates that the content of α -FeOOH in sample decreases as the preparation temperature increases, while the content of rutile TiO_2 increases gradually. As a result, the samples prepared at higher temperature are nearly composed of rutile TiO_2 . This can be attributed to α -FeOOH dissolving in the acidic condition aroused by TiCl_4 hydrolysis at higher temperature.

The crystalline grain size of the particles and weight percentage content of the crystal phase in the samples were estimated according to the Scherrer formula and K -value method, respectively; the results are presented in Table 1. When the temperature is lower than 60 °C, the grain size of the α -FeOOH particles is stable. When the preparation temperature exceeds 60 °C, the grain size of rutile TiO_2 particle is stable, and its weight percentage increases as the temperature rises. Con-

Table 1

Grain size of the (110) plane and percentage content of rutile TiO_2 / α -FeOOH in the photocatalyst samples.

Preparation temperature (°C)	Grain size (nm)		Weight percentage (%)	
	Rutile TiO_2	α -FeOOH	Rutile TiO_2	α -FeOOH
30	—*	48.4	—	100
45	7.7	45.9	20	80
60	4.6	43.9	18	82
75	4.5	—	98	2
90	4.8	—	99	1

*Data were not calculated because of experimental factors, for example, the peak being too weak owing to low content, which may result in error.

versely, the percentage of α -FeOOH obviously decreases as the temperature rises. These results indicate that the grain size of rutile TiO_2 and α -FeOOH particles is related to preparation temperature. The weight percentage of rutile TiO_2 in the samples is positively related to preparation temperature, whereas that of α -FeOOH is negatively related.

3.2. TEM analysis

TEM images of the samples prepared at different temperatures are displayed in Fig. 2. The α -FeOOH rod has a smooth surface and a diameter of about 200 nm, as shown in Fig. 2(a). After reaction with TiCl_4 hydrosol at 30 °C, the surface of the α -FeOOH rod is coated by another substance with variable thickness (Fig. 2(b)). After reaction with TiCl_4 hydrosol at 45 °C, the surface of the α -FeOOH rod is coated with a large number of acicular rutile TiO_2 particles, which form a complete, dense cladding layer with a thickness of 100–150 nm, as shown in Fig. 2(c). When the reaction temperature was increased to 60 °C, the surface of the α -FeOOH rod was coated with many rutile TiO_2 particles (Fig. 2(d)). When the reaction temperature exceeded 75 °C, the microstructure of the sample changed dramatically, forming tubular structures with a length of more than 600 nm and diameter of more than 100 nm. The diameter

Fig. 2. TEM images of α -FeOOH (a), TY-30-2 (b) [23], TY-45-2 (c) [23], TY-60-2 (d) [23], TY-75-2 (e), TY-90-2 (f) prepared at 30, 45, 60, 75, and 90 °C, respectively.

Fig. 3. Microstructures of α -FeOOH support (a) and sample TY-45-2 (b) [23].

of the tube increases with reaction temperature, and its wall is a double layer, in which the inner layer is a complete wall structure, and the outer layer is composed of numerous particles, as illustrated in Fig. 2(e) and (f). The wall of the tubes should be rutile TiO_2 according to the XRD results for the samples fabricated at higher temperature ($\geq 75^\circ\text{C}$). The above results indicate that the samples obtained at higher temperature are rutile TiO_2 tubes. The morphology and diameter of the inner space of the rutile TiO_2 tube is similar to that of the α -FeOOH support. Both TEM and XRD results indicate that the crystal phase and microstructure of the samples is controlled by preparation temperature.

In order to confirm further the relationship between the α -FeOOH support and rutile TiO_2 cladding layer, high resolution transmission electron microscopy (HRTEM) and electron diffraction were characterized on the α -FeOOH support and sample TY-45-2, while the electron diffraction pattern is automatic generated by Fast Fourier Transform (FFT), the results are shown in Fig. 3. The selected area electron diffraction pattern of the α -FeOOH support indicates that it is a single crystal phase, as shown in the inset in Fig. 3(a). The support is highly crystalline and almost all of the (130), (101), and (021) crystal

planes of α -FeOOH can be seen clearly, as indicated in Fig. 3(a). The interplane distances are 0.2188, 0.3174, and 0.2472 nm, as presented in Fig. 3(b), which are close to that of rutile TiO_2 (111), (110), and (101) planes (JCPDS 21-1276), respectively. In addition, a lattice spacing of 0.2658 nm, which is similar to that of the (130) plane of α -FeOOH, is observed (point d in Fig. 3(b)). The electron diffraction pattern of TY-45-2 is shown in the inset at the lower right of Fig. 3(b), and shows the typical concentric ring of polycrystalline diffraction. This indicates that the sample is polycrystalline. The white box in Fig. 3(b) is located at the junction between rutile TiO_2 and α -FeOOH. An enlargement of this region is shown in the inset at the upper right of Fig. 3(b). The dashed line is the boundary between rutile TiO_2 and α -FeOOH, it is obvious that the lattice fringes from (130) plane of α -FeOOH, and (111), (110) plane of rutile TiO_2 cross each other, which implies that there is a coherent relationship between rutile TiO_2 and α -FeOOH phases.

At the microscale, these results prove that the interaction between the α -FeOOH support and rutile TiO_2 coating layer involves chemical bonding rather than physical adsorption. This is because TiCl_4 forms hydroxy intermediate $\text{Ti}(\text{OH})_x$ ($x \leq 4$) during hydrolysis. The hydroxy intermediate reacts with the hydroxyl group of α -FeOOH, causing dehydration condensation to occur during sample preparation. This reaction results in the formation of Ti-O-Fe bonds, which will be located at the interface between rutile TiO_2 and α -FeOOH and form electron trap, which is a kind of cation defect. This process is the main reason why the rutile TiO_2 phase appears at 30°C in this system.

3.3. EDS analysis

EDS results obtained for samples TY-45-2 and TY-90-2 are presented in Fig. 4. Figure 4C–E clearly show that the distribution of O in sample TY-45-2 is uniform, and its distribution outline fits well with the morphology of the sample. The density distribution of Ti and Fe is different: that of Ti is lower at the

Fig. 4. EDS of samples TY-45-2 (A–E) [23] and TY-90-2 (a–e).

Fig. 5. Ti 2p (a), Fe 2p (b), and O 1s (c) XPS profiles of sample TY-90-2.

inner core and higher at the outer side; in contrast, that of Fe is higher at the inner core and lower at the outside. Taking the XRD and TEM results for sample TY-45-2 into account, the α -FeOOH support is coated by rutile TiO_2 to form a composite structure.

Figure 4 c–e indicates that the distribution outlines of O, Ti, and Fe in TY-90-2 are similar to the corresponding elements in TY-45-2, but their density distributions are different. The densities of O and Ti element are relatively high, whereas that of Fe is relatively low. Their similar distribution outlines can be attributed to the dissolving of α -FeOOH in acidic condition during the hydrolysis of TiCl_4 at higher temperature, which allows Fe to enter the TiO_2 lattice as Fe^{3+} cations. In Fig. 4a, the outline of the inner space of the rutile TiO_2 tube is similar to the morphology of the α -FeOOH support, but its size is slightly smaller. This indirectly suggests that the hollow space inside the rutile TiO_2 tube is aroused by α -FeOOH support partially dissolving.

3.4. XPS analysis

High-resolution Ti 2p, Fe 2p, and O 1s XPS profiles of sample TY-90-2 and fitted curves are shown in Fig. 5. Figure 5(a) shows Ti 2p XPS with typical bimodal structure, containing a Ti $2p_{3/2}$ peak at low binding energy and Ti $2p_{1/2}$ peak at high binding energy. Two curves can be drawn by sub-peak fitting, revealing that Ti is present in two chemical states. 458.6 and 464.4 eV correspond to the binding energy of TiO_2 [24,25], while 460.1 and 466.0 eV correspond to the binding energy of TiO_x [26]. These results show that TiO_2 has converted into TiO_x and a low valence state of Ti appears. Formation of TiO_x is related to the formation and rupture of Ti–O–Fe bonds and the thermal diffusion properties of Ti^{4+} and Fe^{3+} during sample preparation [27].

Figure 5(b) shows an Fe 2p XPS profiles of sample TY-90-2. 725 and 711.4 eV correspond to the binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. Therefore, only one chemical state of Fe is present in the sample: Fe^{3+} . The binding energies of the Fe peaks do not deviate obviously from that expected for Fe^{3+} . This is because the difference of electronegativity between Ti and Fe is not evident, and the formation of Ti–O–Fe bonds does not enable the inner electrons of Fe to be shielded by the oxygen bridging bond [28,29].

Figure 5(c) shows the O 1s XPS profiles of sample TY-90-2. Three chemical states of O are present in sample TY-90-2. 529.5 eV corresponds to the binding energy of TiO_2 [30], 531.4 eV corresponds to the binding energy of OH [31], and 533.2 eV is attributed to the binding energy of adsorbed oxygen (H_2O , O_2) because of its high binding energy [31]. Based on peak areas, O 1s exists mainly as lattice oxygen (Ti–O–Ti), which is consistent with the results of Ti 2p XPS, XRD, and TEM. In addition, a certain amount of OH is present on the surface of the rutile TiO_2 tubes according to XPS results. The presence of OH should improve the photocatalytic activity of the sample. In addition, the physical adsorption of oxygen shows that the rutile TiO_2 tubes fabricated by hydrolysis and precipitation should exhibit high activity and adsorption capacity [31,32].

Taking all of the characterization results into account, rutile TiO_2 can effectively coat α -FeOOH at low temperature. The acid solution produced during the hydrolysis of TiCl_4 at high temperature can dissolve α -FeOOH, and then Fe^{3+} can enter into the crystal lattice of rutile TiO_2 tubes as a dopant cation during sample preparation. The structure of the samples changes with preparation temperature. When the temperature is low ($\leq 45^\circ\text{C}$), a composite structure forms. At intermediate temperature (60°C), a mixture of composite and doped structure is produced, and when the temperature is high ($\geq 75^\circ\text{C}$), only the doped structure forms.

3.5. UV-Vis spectral analysis

Figure 6 shows UV-Vis absorption curves of the TY-2 samples, P25, and α -FeOOH. P25 absorbs in the UV region with a peak wavelength of 326 nm, but hardly absorbs in the visible region. α -FeOOH exhibits a weak absorption peak at 315 nm, and a strong, broad one in the visible range centered at 440 nm. Samples TY-30-2, TY-45-2, and TY-60-2 exhibit absorption peaks at 287, 308, and 300 nm, respectively. Their peak positions show a small blue shift compared with that of P25 at 326 nm and α -FeOOH at 315 nm. In addition, the samples absorb over a wide range of 363–452, 362–458, and 365–446 nm for samples TY-30-2, TY-45-2, and TY-60-2, respectively. Their peak positions are red-shifted compared with that of α -FeOOH at 440 nm, and their absorption edges extend to 727, 823, and 821 nm. Samples TY-75-2 and TY-90-2 exhibit strong absorp-

Fig. 6. UV-Vis absorption curves for Y-90-2 (1), TY-75-2 (2), TY-45-2 (3), TY-60-2 (4), α -FeOOH (5), rutile TiO_2 (6), and TY-30-2 (7).

tion peaks at 318 and 310 nm, respectively, and their absorption edges are at 573 and 515 nm, extending into the visible region.

3.6. Photocatalytic degradation of methyl orange

Figure 7 shows the results of the photocatalytic degradation of methyl orange by different TY-2 samples. The photocatalytic degradation of methyl orange by pure rutile TiO_2 is poor. After irradiation for 180 min, only 10% of methyl orange is degraded. The photocatalytic degradation of methyl orange by the five TiO_2/α -FeOOH samples can be divided into three categories according to their characteristics after illumination for 60 min. (1) The degradation effect increases as the illumination time increases such as sample TY-45-2. (2) When the illumination time is between 60 and 150 min, the degradation proceeds smoothly, and then increases as the illumination time increases further. Samples TY-30-2 and TY-90-2 fall into this category. (3) The degradation effect increases continuously as illumination time progresses. Samples TY-60-2 and TY-75-2 are typical of this category. The degradation of methyl orange by TY-60-2 reaches 79.7% after illumination for 180 min.

Sample TY-30-2 is a composite material of TiO_2 and α -FeOOH, where TiO_2 particles are distributed on the surface of α -FeOOH and do not form a complete cladding (Fig. 2(b)). As a result, its photocatalytic degradation performance is poor. Sample TY-45-2 is a composite material of TiO_2 and α -FeOOH, where acicular TiO_2 particles are distributed over the entire surface of α -FeOOH to form a core-shell structure (Fig. 2(c)). Electron traps form at the interface between TiO_2 and α -FeOOH, which are a kind of cation defect. This defect can effectively hinder the recombination of photogenerated electron-hole pairs, improving the photocatalytic efficiency of the catalyst [31–35]. Chen et al. [36] reported that many unsaturated oxygen atoms exist on the surface of nanoscale iron oxides. The same is true for the surface of nanoscale titanium oxide too. As a result, the binding energy of Ti–O–Fe at the interface between TiO_2 and α -FeOOH is strong. In addition, compared with α -FeOOH, this sample contains more dislocations

Fig. 7. Photodegradation of methyl orange by samples irradiated with two lamps (wavelength range of 200–800 nm).

and surface defects (e in Fig. 3(b)), which can behave as active sites during photocatalysis. Therefore, the photocatalytic performance of TY-45-2 is improved compared with that of TiO_2 alone.

TiO_2 particles of the sample TY-60-2 were distributed over the entire surface of α -FeOOH to form a core-shell structure (Fig. 2(d)). XPS results for this sample indicated iron ions were doped in the rutile TiO_2 lattice, so sample TY-60-2 is a mixture of both composite and doped structures. Fe^{3+} doped into the TiO_2 crystal lattice causes it to distort. Considering energy band theory, the interaction between the t_{2g} level of Ti^{4+} and p - π level of O^{2-} in the lattice results in the formation of π and π^* bands, which are the valence and conduction bands, respectively, of the TiO_2 semiconductor. A new d band will form in the band gap of TiO_2 when low valence Fe^{3+} replaces Ti^{4+} in the TiO_2 lattice. The d band does not overlap with the π^* band because the d level of Ti^{4+} lies lower than the π^* band in the lattice. As a result, many separate impurity bands were formed in the forbidden band, which can overlap with the conduction band of TiO_2 . In this case, electrons will be photogenerated by the semiconductor after absorption of a relatively small amount of energy, and its response range to light will widen, so its photocatalytic activity will be enhanced.

These results imply that the photocatalytic activity and efficiency of the sample with a mixed composite/doped structure is improved because it can prolong the lifetime of photogenerated holes and electrons; in other words, the doped and composite structures coordinate well.

This is the main reason why the absorption edge of TY-60-2 extends into the visible region, and why its photocatalytic degradation performance is higher than that of the other samples. Besides, the structure of samples TY-75-2 and TY-90-2 is tubular and doped with iron. The photocatalytic performance of these samples is better than that of samples with a core-shell structure, and similar to that of the sample with a mixture of composite and doped structures, which is correlated to its structural characteristics. In summary, the photocatalytic performance of a TiO_2 -based photocatalyst is not only related to its crystal phase, but also correlated to its structure.

4. Conclusions

TiO₂/α-FeOOH photocatalysts with controlled crystal phase and microstructure were prepared by hydrolysis and precipitation at specific reaction temperatures. At low temperature, a composite material with core-shell structure containing rutile TiO₂ as a shell and α-FeOOH as a core was fabricated. At higher temperature, Fe³⁺-doped rutile TiO₂ tubes formed, and at intermediate temperature, the resulting photocatalyst contained a mixture of composite and doped structures. Combining rutile TiO₂ with α-FeOOH significantly improved the optical absorption of the samples, and the absorption edge of Fe³⁺-doped rutile TiO₂ tubes was extended to the visible region. Among the above three different structures, the sample with both composite and doped structures exhibits the highest activity, while the composite structure exhibits poor activity. In summary, the structure of the photocatalysts affects its photocatalytic performance for degradation of methyl orange.

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Graphical Abstract

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Preparation and photocatalytic activity of rutile TiO₂ and goethite composite photocatalysts

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The structure of rutile TiO₂ and α-FeOOH composite photocatalysts can be controlled by adjusting reaction temperature, and their photocatalytic activity is maximized when they possess a core-shell structure with Fe³⁺ doping.

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二氧化钛与针铁矿复合光催化材料的制备与光催化性能

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摘要: 以四氯化钛为钛源, 针铁矿(α -FeOOH)为载体, 采用水解沉淀法制备了金红石相二氧化钛(Ti_2O_3)与 α -FeOOH的复合光催化材料, 并采用X射线衍射、扫描电子显微镜、透射电子显微镜、X射线能量散射谱和X射线光电子能谱对样品进行了表征。结果表明, 低温下, 金红石相 Ti_2O_3 包覆于 α -FeOOH表面, 并形成复合结构; 较高温下, 铁离子进入金红石相 Ti_2O_3 晶格, 并形成铁掺杂金红石相 Ti_2O_3 纳米管; 中温下, 样品兼有复合和掺杂两者特征。在室温下以甲基橙为降解对象, 采用钨灯+氙灯(波长200~800 nm)为光源, 对样品的光催化活性进行了测试。结果表明, 样品对甲基橙的光催化降解效果良好; 与纯 α -FeOOH和金红石相 Ti_2O_3 相比, 不同结构样品的光催化活性均有所提高, 其中, 复合兼掺杂型样品的光催化活性最高。由此可见, 与 α -FeOOH复合和铁掺杂是提高 Ti_2O_3 光催化活性的有效途径。

关键词: 二氧化钛; 针铁矿; 复合材料; 光催化性能; 甲基橙

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1. 前言

如何解决环境保护问题是当今社会所面临的一个重要课题。在未来二十年中, 环境污染治理将成为最急于优先解决的全球性问题^[1~3]。应用半导体光催化材料治理环境污染是最有前途的技术方法之一^[4~6]。在众多半导体光催化剂材料中, 纳米 TiO_2 具有无毒、光化学性质稳定、催化效率高、氧化能力强, 且无二次污染等特点, 因而广泛应用于光催化处理水和空气等环境污染问题中^[7,8]。

然而, 纳米 TiO_2 半导体光催化材料在实际应用中存在明显的不足。一方面, TiO_2 带隙较宽(锐钛矿可达3.2 eV), 其吸收阈值为387.5 nm, 只能吸收紫外光, 在可见光范围基本没有响应, 对太阳光利用率低(约3%~5%); 另一方面, TiO_2 光生载流子的寿命短, 在纳秒(ns)到皮秒(ps)时间范围内, 复合率高。从而大大降低了纳米 TiO_2 的光催化效率。因此, 如何提高光催化效率是当今纳米 TiO_2 光催化材料应用研究的热点和难点之一, 也是其走向实际应用的关键。

国内外学者通过控制晶体结构和表面物化性质^[9], 如掺杂金属离子^[10~12] (如 Fe^{3+} , Cr^{3+} , Mn^{2+} 和 Co^{2+} 等具有全充满或半充满电子构型的过渡金属离子)和非金属元素(如N, S, F和V等)^[13~15], 及 TiO_2 与其它带隙较窄的半导体复合等途径, 以减小 TiO_2 光催化材料的带隙, 并降低光生载流子复合率。近年来 $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ^[16], $\text{TiO}_2/\text{SiO}_2$ ^[17], TiO_2/WO_3 ^[18], TiO_2/ZnO ^[19]等多相复合体系已得到广泛研究。在众多带隙较窄的金属氧化物半导体中, α -FeOOH因带隙较窄(2.6 eV), 可作为 TiO_2 的载体之一。若将它与 TiO_2 复合可减小光催化材料的禁带宽度, 使复合材料的光响应范围扩展至可见光^[20,21]。此外, α -FeOOH也可为金属离子掺杂提供 Fe^{3+} , 以提高 TiO_2 光催化材料的性能。

人们对 TiO_2/α -FeOOH光催化材料进行了深入的研究。梁凯等^[20]利用水解沉淀法制备了核壳结构的 $\text{TiO}_2/\text{FeOOH}$ 复合材料, 复合后产生明显的协同效应, 光催化降解有机物的能力明显提高。Rawal等^[21]在研究中发现, $\text{TiO}_2/\text{FeOOH}$ 纳米复合材料在可见光($\lambda \geq 420$ nm)下可将气态异丙醇降解为 CO_2 , 表现出较高的光催化降

解效率。但现有文献报道中,很少涉及制备参数与 $\text{TiO}_2/\alpha\text{-FeOOH}$ 光催化材料降解有机物性能的关系,尤其是制备参数与其微结构的关系以及微结构与性能的关联。

本文以四氯化钛(TiCl_4)为前驱体, $\alpha\text{-FeOOH}$ 为载体,制备复合型 and 掺杂型 $\text{TiO}_2/\alpha\text{-FeOOH}$ 光催化材料,考察了制备条件对其光催化降解甲基橙活性的影响,探索了复合型和掺杂型光催化材料性能与其结构的关联性。

2. 实验部分

2.1. 样品的制备

以市售 TiCl_4 (上海美心化工股份有限公司,化学纯)为前驱体,在 $-10\sim 0\text{ }^\circ\text{C}$ 冰水浴中将其缓慢滴加到去离子水中,两者体积比为1:2,并充分搅拌,滴加完毕后持续搅拌2 h,待体系转变成浅黄绿色溶胶后,于室温老化10~14 h,即得 TiCl_4 水溶胶^[22]。

在搅拌下将适量去离子水滴到上述 TiCl_4 水溶胶中,获得稀释后的水溶胶。按Fe/Ti摩尔比为1:1将 $\alpha\text{-FeOOH}$ (升华集团德清华源颜料有限公司)分散到上述稀释的溶胶中,再将其均匀地分为5等份,分别在30, 45, 60, 75和 $90\text{ }^\circ\text{C}$ 搅拌反应2 h。静置、抽滤和水洗,如此循环数遍,直至无氯离子检出,然后在 $80\text{ }^\circ\text{C}$ 干燥12 h,即得TY-30-2, TY-45-2, TY-60-2, TY-75-2和TY-90-2样品。

2.2. 样品的表征

采用X射线衍射(XRD)、透射电子显微镜(TEM)、X射线能量散射谱(DES)和X射线光电子能谱(XPS)对样品的晶相组成、形貌、微结构、化学组成和价态进行了表征。其中,XRD分析在荷兰PANalytical公司X'Pert PRO型X射线衍射仪上进行,Cu K_α 射线($\lambda = 0.1541\text{ nm}$),电压40 kV,电流40 mA,步长 0.03° ,范围 $15^\circ\sim 85^\circ$;TEM为荷兰Philips-FEI公司Tecnai G2 F30 S-Twin型,300 kV;XPS表征在日本岛津公司Kratos AXIS Ultra DLD型光电子能谱仪上进行。

2.3. 性能测试

紫外-可见(UV-Vis)光吸收性能测试:按体积比为3:7配制乙醇/去离子水混合液,将纯金红石相 TiO_2 、 $\alpha\text{-FeOOH}$ 和样品分散于其中,配制浓度为 10^{-5} g/ml 的半透明溶液,超声5 min后离心并取上层清液,在Shimadzu UV1800紫外可见分光光度计(UV-Vis)上进行光吸收性能测试,扫描范围200~800 nm。

光催化反应在自制的装置中进行。在室温下以钨灯+氙灯(波长200~800 nm)为降解光源,称取载体、纯金红石相 TiO_2 和各种样品各0.005 g,在避光条件下将它们加

到初始浓度为20 mg/L甲基橙溶液中,超声5 min,使之达到吸附-脱附平衡。然后在上述光源照射下分别进行光催化降解反应,并在0, 30, 60, 90, 120, 150和180 min时取一定体积的已降解悬浊液,经高速离心分离后取上层清液,在紫外可见分光光度计上进行吸光度测试,吸光度检测波长为462 nm。

3. 结果与讨论

3.1. XRD结果

图1为各样品的XRD谱。由图可见,随着制备温度的升高,金红石相 TiO_2 (PDF 21-1276)特征衍射峰($2\theta = 27.42^\circ$)逐渐增强, $\alpha\text{-FeOOH}$ (PDF 29-0713)衍射峰则逐渐减弱;在高温($\geq 75\text{ }^\circ\text{C}$)制备的样品中, $\alpha\text{-FeOOH}$ 衍射峰基本消失,尤其是 $2\theta = 21.224^\circ$ 处特征衍射峰彻底消失,仅出现金红石相 TiO_2 的衍射峰。这说明随着制备温度的升高,所得样品中 $\alpha\text{-FeOOH}$ 逐渐减少,金红石相 TiO_2 逐渐增加,高温下样品基本由金红石相 TiO_2 组成。这可能是由于高温下 TiCl_4 水解产生的酸强度大,致使 $\alpha\text{-FeOOH}$ 溶解所致。

利用谢乐公式和 K 值法计算了样品晶粒度大小和相对百分含量,结果见表1。可以看到,当制备温度高于 $60\text{ }^\circ\text{C}$ 时,所得样品中金红石相 TiO_2 的粒径基本稳定,其百分含量随制备温度升高而增加。对于 $\alpha\text{-FeOOH}$,当制备温度低于 $60\text{ }^\circ\text{C}$ 时其粒径基本稳定;高于 $75\text{ }^\circ\text{C}$ 时,其百分含量随制备温度的升高显著降低。由此可见,金红石相 TiO_2 和 $\alpha\text{-FeOOH}$ 的粒径大小与制备温度有关,样品中金红石相 TiO_2 的含量与制备温度呈正相关,而 $\alpha\text{-FeOOH}$ 的含量与制备温度呈负相关。

3.2. TEM结果

图2为各样品的TEM照片。由图可见,载体 $\alpha\text{-FeOOH}$ 呈棒状,表面光滑,直径200 nm左右; $30\text{ }^\circ\text{C}$ 时它与 TiCl_4 水溶胶反应后,其表面包覆一些其它物质,且包覆厚度不均匀。 $45\text{ }^\circ\text{C}$ 反应后 $\alpha\text{-FeOOH}$ 表面包覆大量针状金红石相 TiO_2 颗粒,且形成厚度100~150 nm的完整致密包覆层;当反应温度升至 $60\text{ }^\circ\text{C}$ 时, $\alpha\text{-FeOOH}$ 表面包覆了较多的金红石相 TiO_2 颗粒;至 $75\text{ }^\circ\text{C}$ 时,样品的微结构发生了显著变化,形成了明显的管状结构,管内空长大于600 nm,直径大于100 nm,且随着制备温度的升高而增大,管壁具有明显的双层结构,即结构较为完整的层状壁及其外侧的颗粒层。结合高温($\geq 75\text{ }^\circ\text{C}$)制备样品的XRD结果可认为,构成样品管壁的应为金红石相 TiO_2 。上述结果表明,高温时制得的样品为 TiO_2 管。将管内空

腔与载体 α -FeOOH的形貌和大小对比, 两者的吻合度很好. 这应是由于高温时, α -FeOOH溶解于 TiCl_4 水解所产生的酸性溶液中所致. 由此说明, 温度对所制样品微结构的影响很大. 综上可见, 样品形貌、晶相组成和微结构特征与其制备温度密切相关.

为进一步确认载体 α -FeOOH与金红石相 TiO_2 包覆层之间的关系, 对 α -FeOOH和TY-45-2样品进行了高分辨率透射电镜(HRTEM)及电子衍射的表征, 其中电子衍射图是由傅里叶变换(FFT)生成的, 结果见图3. 可以看出, α -FeOOH为单晶结构, 晶粒完整, 对应的晶面如图3(a)标记所示, 其FFT为对称性良好的六边形, 如图3(a)中嵌入图所示. 图3(b)中a, b和c处的晶格间距分别为0.2188, 0.3174和0.2472 nm, 分别与金红石相 TiO_2 (111), (110)和(101)晶面(JCPDS 21-1276)的间距接近, d处晶格间距为0.2658 nm, 与 α -FeOOH (130)晶面接近. 图3(b)右下嵌入图为TY-45-2样品的电子衍射照片, 为典型的同心圆环多晶衍射. 这说明样品由多晶组成. 图3(b)白色方框位于金红石相 TiO_2 与 α -FeOOH载体的交界处, 右上角嵌入图是对其的局部放大, 其中的折线为界面位置. 可以看出, α -FeOOH(130)面与金红石相 TiO_2 的(111)和(110)面的晶格条纹相互交叉. 这说明两相结构在准周期面内形成了良好的共格关系. 这从微观角度证明金红石相 TiO_2 在 α -FeOOH表面形成的包覆层不是简单的物理吸附, 而是形成了键合作用.

这是由于 TiCl_4 水解过程中会形成带羟基的中间产物 $\text{Ti}(\text{OH})_x$ ($x \leq 4$), 它与 α -FeOOH的羟基发生脱水缩合, 导致两者间形成 Ti-O-Fe , 它位于两相界面处, 并产生电子阱, 即阳离子缺陷. 这可能也是30 °C所制样品中出现金红石相 TiO_2 的主要原因.

3.3. EDS结果

TY-45-2和TY-90-2样品的EDS结果如图4所示. 图4 A和B为TY-45-2样品的形貌, C, D和E为EDS元素分布图. 图4 a和b为样品TY-90-2的形貌, c, d和e为EDS元素分布图. 从图4 C, D和E中可以看出, 样品TY-45-2中O元素分布较均匀, 与样品形貌轮廓的吻合度较高. Ti元素和Fe元素的密度分布相反: Ti元素主要集中在外侧, 内侧较少, Fe元素主要集中在内侧, 外侧较少. 结合XRD和TEM结果可充分说明, TY-45-2样品中 α -FeOOH载体被金红石相 TiO_2 包裹, 并形成了较为完整的复合结构.

另外, TY-90-2样品中O, Ti和Fe的元素分布形貌较相似, 只是强度上有所差异. 其中, O和Ti元素分布密度相对较强, Fe元素分布密度相对较弱. 这些元素分布轮

廓较相似, 这可能是由于, 高温下 α -FeOOH在 TiCl_4 水解产生的酸性溶液中溶解, Fe以 Fe^{3+} 形式进入 TiO_2 的晶格内所致. 图4a中, 纳米管的内空形貌与载体 α -FeOOH相似, 仅直径略小. 这可间接证明纳米管的空腔是 α -FeOOH溶解后的残留.

3.4. XPS结果

TY-90-2样品表面的Ti 2p, Fe 2p及O 1s的高分辨扫描XPS谱及分峰拟合图见图5. 由图5(a)可见, Ti 2p XPS谱线均为典型的双峰结构, 即由结合能较低的Ti 2p_{3/2}峰和结合能较高的Ti 2p_{1/2}峰组成. 通过分峰拟合, 均可得到2组对峰. 说明Ti元素存在2种化学状态, 即458.6和464.4 eV, 对应于 TiO_2 的结合能^[24,25], 以及460.1和466.0 eV, 对应于 TiO_x 的结合能^[26]. 可见 TiO_2 向 TiO_x 转换出现了低价态Ti, 这可能与反应过程中Ti-O-Fe键的形成与断裂及 Ti^{4+} 与 Fe^{3+} 的热扩散性质有关^[27].

图5(b)是TY-90-2样品的Fe 2p XPS窄扫描谱图. 由图可见, Fe元素只存在1组对峰, 即711.4和725.0 eV, 分别对应于Fe 2p_{3/2}和Fe 2p_{1/2}. 这说明Fe元素只有1种化学状态, 即 Fe^{3+} . 从结合能大小看, Fe元素对峰的结合能位置并未发生太多的偏移. 由于Ti与Fe的电负性相差不大, Ti-O-Fe键的形成并未使Fe原子内层电子因桥氧键的存在而受到明显的屏蔽作用^[28,29], 因此结合能没有发生太大的改变.

图5(c)为TY-90-2样品的O 1s分峰拟合图. 由图可见, O元素存在3种化学状态, 其中529.9 eV对应于 TiO_2 的结合能^[30], 531.4 eV对应于OH的结合能^[31], 533.2 eV的结合能较大, 可归结为吸附氧(H_2O , O_2)的结合能^[31]. 从峰面积可以看出, O 1s主要以晶格氧Ti-O-Ti形式存在. 这与前文结果一致. 此外, 金红石相 TiO_2 纳米管表面存在一定量的OH, 因而有利于提高样品的光催化活性; 物理吸附氧的存在则从侧面说明了采用水解沉淀法制备的金红石相 TiO_2 纳米管具有很高的活性和较强的吸附能力, 从而有利于样品光催化活性的提高^[31,32].

综上所述, 在低温条件下金红石相 TiO_2 与 α -FeOOH通过复合的方式可形成良好的包覆结构; 高温时 TiCl_4 水解产生的酸性溶液能将 α -FeOOH溶解, 且 Fe^{3+} 以掺杂形式进入了金红石相 TiO_2 纳米管的晶格中. 上述结果说明, 随着制备温度的改变, 样品结构发生变化, 低温(≤ 45 °C)下为复合结构, 中温(60 °C)为复合兼掺杂结构, 较高温(≥ 75 °C)为掺杂结构.

3.5. UV-Vis结果

图6为P25和所制各样品的UV-Vis谱. 由图可知, P25

在326 nm处出现吸收峰,但在可见光区几乎没有吸收峰; α -FeOOH除了在315 nm处出现较弱的吸收峰外,在440 nm处还有个较明显的吸收峰,其半峰宽较宽,吸收的范围较大;TY-30-2, TY-45-2和TY-60-2样品分别在287, 308和300 nm处出现吸收峰,其峰位相对于P25和 α -FeOOH略有蓝移.此外,这3个样品分别在363~452, 362~458和365~446 nm处出现了范围较宽的吸收.上述吸收峰相对于 α -FeOOH有所红移,且吸收边带均有拓展,分别延伸到727, 823和821 nm左右. TY-75-2和TY-90-2在318和310 nm处有较强的吸收峰,吸收边带为573 nm和515 nm左右,已拓展到了可见光区.

3.6. TY-2样品光催化降解甲基橙

图7为各TY-2样品光催化降解甲基橙的反应性能.由图可知,纯金红石相TiO₂的光催化降解效果较差,反应180 min后,甲基橙仅降解10%左右.所制5个样品的光催化性能依据其光照60 min后的曲线特征可分为三种类型:(1)随着光照时间的延长,降解效果平稳增加,如TY-45-2样品;(2)当光照时间介于60~150 min时,降解效果平稳增加,继续延长光照时间,降解效果增加明显,如TY-30-2和TY-90-2样品;(3)随着光照时间的延长,降解效果持续增强,如和TY-75-2样品,其中TY-60-2样品经180 min光照后对甲基橙的降解率高达79.7%.

TY-30-2样品为TiO₂与 α -FeOOH复合物, TiO₂颗粒分布于 α -FeOOH表面,且未形成完整的包覆结构(如图2(b)所示),因此,其光催化降解性能较差. TY-45-2样品为TiO₂与 α -FeOOH复合物, TiO₂针状颗粒分布于 α -FeOOH表面,并形成较为完整的核壳结构(如图2(c)所示),如前所述, TiO₂与 α -FeOOH复合后,在两相界面处可产生电子阱,即阳离子缺陷.这种缺陷能有效地阻碍光生电子-空穴的复合,从而提高催化剂的光催化反应效率^[31~35]. 陈金媛等^[36]发现,纳米级铁氧化物的表面存在大量配位不饱和的氧原子,因此,在纳米级钛氧化物表面也可能存在这种情况,致使两者界面处的Ti-O-Fe键结合能较强.此外,与 α -FeOOH相比,样品内部存在大量的位错、面缺陷等(如图3(b)中e处所示),也可成为样品的光催化活性位,因此其光催化降解性能较好.

TY-60-2样品中TiO₂颗粒分布于 α -FeOOH表面,且

形成较为完整的核壳结构(见图2(d)),铁离子掺杂入金红石相TiO₂晶格内,因此, TY-60-2样品兼有复合和掺杂结构的特征,以及核壳结构复合和掺杂材料的性能. Fe³⁺掺杂进入到TiO₂晶体内,必导致晶格参数发生畸变.结合能带理论,晶格中Ti⁴⁺的 t_{2g} 轨道与氧离子的 p - π 轨道相互作用形成了 π 与 π^* 能带, π 能带为半导体TiO₂的价带, π^* 能带为半导体TiO₂的导带.当低价的Fe³⁺取代TiO₂晶格中Ti⁴⁺时,在TiO₂带隙中形成新的 d 能带.由于晶格中Ti⁴⁺的 d 轨道在 π^* 能带下方附近,所以新形成的 d 能带不能与 π^* 能带交迭,故在禁带中形成了许多分离的杂质中间能级, π^* 能带与杂质能级交迭,分离的杂质中间能级将合并成杂质禁带并与TiO₂导带重叠.这时半导体光生电子在吸收较低能量时即可发生跃迁,光响应范围增大,光催化活性增强.

上述结果说明,复合兼掺杂样品的光催化活高,又可延长光生空穴与电子的寿命,提高其光催化效率,即掺杂结构与复合结构能够很好地协同.这是TY-60-2样品的吸收边带拓展到可见光,也是其光催化性能好于其它样品的原因.另外, TY-75-2和TY-90-2样品具有管状结构和铁离子掺杂特征,其光催化降解性能好于核壳结构复合样品,与复合兼掺杂样品相近,但性能较差,较好地体现了其结构特征.

综上所述,样品光催化降解有机物性能不仅与其晶相组成有关,更与其结构相关.

4. 结论

在水解沉淀法制备TiO₂/ α -FeOOH光催化材料的过程中,通过控制反应温度可较好地调控其晶相组成和微结构特征:低温时可制得以金红石相TiO₂为壳, α -FeOOH为核的核壳结构复合材料;较高温时则得到Fe³⁺掺杂金红石相TiO₂管;中温时所得光催化材料具有复合和掺杂两种结构特征.将金红石相TiO₂与 α -FeOOH复合,能明显提升样品的光学性能, Fe³⁺掺杂金红石相TiO₂纳米管的吸收边带可拓展到可见光区.在上述三种结构的样品中,光催化降解有机物性能较差的是复合结构样品,最好的是复合兼掺杂结构样品,即样品光催化性能与结构密切相关.