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Article

Enhanced visible-light photocatalytic oxidation capability of carbon-doped TiO₂ via coupling with fly ash

Ning An ^a, Yuwei Ma ^b, Juming Liu ^{a,*}, Huiyan Ma ^a, Jucai Yang ^c, Qiancheng Zhang ^{a,#}^a Key Lab of Industrial Catalysis of the Inner Mongolia Autonomous Region, School of Chemical Engineering, Inner Mongolia University of Technology, Huhhot 010051, Inner Mongolia, China^b School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China^c School of Energy and Power Engineering, Inner Mongolia University of Technology, Huhhot 010051, Inner Mongolia, China

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ABSTRACT

A carbon-doped TiO₂/fly ash support (C-TiO₂/FAS) composite photocatalyst was successfully synthesized through sol impregnation and subsequent carbonization. The carbon dopants were derived from the organic species generated during the synthesis of the C-TiO₂/FAS composite. A series of analytical techniques, such as scanning electron microscopy (SEM), attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), were used to characterize the properties of the prepared samples. The results indicated that C-TiO₂ was successfully coated on the FAS surface. Coupling between C-TiO₂ and FAS resulted in the formation of Si–O–C and Al–O–Ti bonds at their interface. The formation of Si–O–C and Al–O–Ti bonds gave rise to a positive shift of the valence band edge of C-TiO₂ and enhanced its oxidation capability of photogenerated holes as well as photodegradation efficiency of methyl orange. Moreover, the C-TiO₂/FAS photocatalyst exhibited favorable reusability and separability. This work may provide a new route for tuning the electronic band structure of TiO₂.

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1. Introduction

Semiconductor photocatalysis is regarded as one of the best technologies for using solar energy to eliminate organic pollutants, and titanium dioxide (TiO₂) represents the primary photocatalyst employed in this field [1,2]. TiO₂ has many excellent properties, such as non-toxicity, low cost, anti-photocorrosion ability, etc. [2]. However, the poor photocatalytic activity of pristine TiO₂ under visible-light irradiation severely limits its use in practical applications. Hence, numerous efforts have

been directed to enhancing the absorption and photocatalytic activity of TiO₂ under visible-light [3–13]. Among the investigated systems, carbon doping of TiO₂ has been demonstrated to be an effective approach for introducing visible-light absorption and enhancing the corresponding photocatalytic activity [14–18]. Previous results have shown that carbon doping could effectively narrow the bandgap of TiO₂ and promote the separation of photogenerated electron-hole pairs [15–19].

Fly ash (FA) is a solid waste produced from the combustion of raw coal in fossil power plants. Irregular accumulation and

* Corresponding author. E-mail: liujuming@imut.edu.cn

Corresponding author. E-mail: jzhang@imut.edu.cn

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inappropriate disposal of FA lead to occupation of vast areas of land, with serious pollution of soil, air, water, and even organisms [20]. Therefore, the recycling of FA is attracting considerable interest from numerous research groups [21]. In addition, FA also exhibits advantageous properties such as non-toxicity, low cost, and chemical/physical stability; hence, it has been proposed as a promising catalyst support material [20,21].

The use of FA as a support material to increase the photocatalytic efficiency of TiO_2 has recently been reported. For example, Visa et al. [22,23] prepared a TiO_2 -FA composite using a hydrothermal method. Their results showed that the obtained composite enabled the efficient simultaneous removal of pollutants from single-, bi-, and tri-pollutant solutions. Saud et al. [24] prepared FA-doped TiO_2 nanofibers by the electrospinning method. The results indicated that the incorporation of FA into TiO_2 nanofibers significantly enhanced the photocatalytic and antibacterial performances. Wang et al. [25] used chitosan-carbonized fly ash (FAC-CS) as a buoyant support to prepare an iron and nitrogen co-doped TiO_2 /FAC-CS composite photocatalyst. Due to its floating ability on the surface of water, the obtained Fe-N- TiO_2 /FAC-CS composite could fully utilize the sunlight spectrum, especially in the visible range and exhibited high activity in the photocatalytic degradation of diesel. Wang et al. [26] prepared a low-cost zeolite fly ash bead/ TiO_2 (ZFABT) photocatalyst with high adsorbability and photocatalytic performance. The results of their study indicated that ZFABT is beneficial for improving the photocatalytic effects of TiO_2 . At the optimal preparation conditions, ZFABT samples exhibited a higher adsorption capacity and photocatalytic efficiency for RhB removal compared to unsupported TiO_2 or inactivated support/ TiO_2 samples.

Although various TiO_2 /FA composite photocatalysts have been prepared through different synthesis routes, to the best of our knowledge, carbon-doped TiO_2 /FA composites have not been synthesized or investigated to date. Moreover, the mechanism by which FA promotes the photocatalytic activity of TiO_2 is still not well understood. In particular, the electronic band structure at the surface/interface of the TiO_2 /FA composite photocatalyst and its influence on the visible-light photocatalytic activity have not been systematically investigated to date.

In this work, a facile sol impregnation and carbonization method was used to synthesize a carbon-doped TiO_2 /fly ash support (C- TiO_2 /FAS) photocatalyst. The carbon dopants, derived from the organic species generated during the synthesis process, were simultaneously incorporated into the TiO_2 lattice [19]. A series of analytical techniques were used to characterize the properties of the obtained samples. In particular, the surface/interface chemical states of the C- TiO_2 /FAS catalyst and their effects on the electronic band structure as well as the photocatalytic activity of C- TiO_2 were investigated in detail. The possible band structure and photocatalytic mechanism of C- TiO_2 /FAS were also discussed.

2. Experimental

2.1. Materials

Raw FA was collected from a coal-fired power plant. All chemicals used in this study were of analytical grade. Nitric acid and tetrabutyl titanate (TBT) were purchased from Beijing Chem. Plant (China). Anhydrous ethanol and glacial acetic acid were obtained from Tianjin Tiantai Fine Chem. Co., Ltd. (China). All chemicals were used without further purification.

2.2. Photocatalyst preparation

2.2.1. Support preparation

Some residual impurities in the raw FA may affect the photocatalytic performance of the prepared samples. Acid leaching and calcination treatments can be used to refine the raw FA. After sieving through a 160-mesh sieve ($< 96.5 \mu\text{m}$), the sieved FA was immersed in a 10 wt% HNO_3 solution for 12 h. After pretreatment, the resulting suspension was filtered. The obtained cake was washed and dried at 100°C and then calcined at 500°C for 3 h, yielding the FAS powder.

2.2.2. Photocatalyst preparation

The C- TiO_2 /FAS photocatalyst was prepared through a sol impregnation and carbonization process. In the synthesis process, solution A was prepared by dissolving 7 mL TBT into 5 mL anhydrous ethanol with stirring. Solution B, which consisted of 5 mL anhydrous ethanol, 7 mL glacial acetic acid, and 3 mL distilled water, was slowly added into solution A with continuous stirring to obtain a Ti sol. Subsequently, the FAS was immersed in the obtained Ti sol under stirring. Then, the mixture was heated at 70°C with constant stirring until the gel formed. The FAS coated with the gel was dried at 90°C for 12 h and then carbonized at 300°C in a N_2 atmosphere for 2 h, to obtain the C- TiO_2 /FAS sample. For comparison, pure C- TiO_2 particles were also prepared by the same approach, without adding FAS.

2.3. Photocatalyst characterization

X-ray diffraction (XRD) patterns were recorded by an Empyrean X-ray diffractometer with $\text{Cu } K_\alpha$ radiation. The surface morphology was investigated by scanning electron microscopy (SEM) using a JSM-6701F field emission microscope. Nitrogen adsorption/desorption measurements at -196°C were performed using a Quadrasorb SI-MP apparatus. The surface area was calculated using the Brunauer-Emmett-Teller (BET) method within a relative pressure (P/P_0) range of 0.05–0.30. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo ESCALAB 250 spectrometer with Al K_α radiation as excitation source. In order to analyze the surface chemical state of the obtained samples, the publicly available XPSPEAK v4.1 software package was used to perform a curve fitting of the raw data corresponding to the Si 2p, Al 2p, Ti 2p, O 1s, and C 1s high-resolution spectra. Fourier-transform infrared (FTIR) spectra were collected using a Perkin Elmer Frontier spectrometer with an attenuated total reflection (ATR) accessory. Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) measurements were recorded by a Shimadzu UV-3600 spectrometer. Photoluminescence (PL) spectra were measured at room temperature on a Shimadzu RF-5301PC

spectrometer. The excitation wavelength was 450 nm, whereas the excitation and emission slit widths were set at 10 nm. The time-resolved transient photoluminescence spectrum was recorded using an Edinburgh Instruments FLS980 fluorescence spectrometer at an excitation wavelength of 350 nm.

2.4. Photocatalytic performance

The photocatalytic performance of the catalysts was evaluated by monitoring the degradation of methyl orange (MO) under visible-light irradiation. A 20 W LED lamp (450 nm) with a cut-off filter ($\lambda \geq 420$ nm) served as the light source (Fig. S1, Supporting Information). In a typical run, 30 mL of MO solution (20 mg/L) was mixed with 0.1 g of C-TiO₂/FAS. After the adsorption equilibrium was reached, the mixture was injected into a quartz photoreactor and illuminated by the LED light source described above. A small amount of the solution sample was collected every 30 min and subsequently filtered through a millipore filter (pore size 0.22 μm). Then, the absorbance of the filtrate was measured by a TU1901 UV-Vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China). The MO degradation efficiency was calculated from the absorbance at 464 nm, which is the wavelength corresponding to the maximum MO absorption. The degradation efficiency (percentage) was estimated as $(A_0 - A_t) / A_0 \times 100\%$, where A_0 and A_t are the absorbances of the MO solution before irradiation (corresponding to the initial MO concentration) and at different irradiation times, respectively. The photodegradation performances of the bare FAS and pure C-TiO₂ particles were also measured and compared with those of the C-TiO₂/FAS composite.

3. Results and discussion

3.1. Morphology and structure

Fig. 1 shows the XRD patterns of bare FAS, pristine C-TiO₂, and C-TiO₂/FAS with a calculated loading of 45% (by mass). The XRD pattern of the FAS sample confirms that quartz and mullite are its main components [27]. The curve measured for

Fig. 1. XRD patterns of different samples.

the C-TiO₂/FAS catalyst shows a marked decrease in the intensity of the diffraction peaks correlated with quartz and mullite, together with the appearance of the diffraction peaks of TiO₂, which indicates that C-TiO₂ was coated on the surface of FAS and masked its XRD signal. The XRD pattern of C-TiO₂ can be ascribed to TiO₂ crystals with tetragonal anatase phase (JCPDS 99-0008), while no other polymorphs of TiO₂ such as rutile and brookite are found. In addition, the weak intensity and broadened full width at half maximum (FWHM) of the diffraction peaks of C-TiO₂ and C-TiO₂/FAS reveal their poor crystallinity and very small crystal size. Therefore, it is reasonable to conclude that C-TiO₂ and C-TiO₂/FAS contain considerable amounts of bulk and/or surface defects.

The SEM images of FAS and C-TiO₂/FAS are shown in Fig. 2. As shown in Fig. 2(a), FAS exhibits two types of morphologies: spherical particles and amorphous agglomerates of spherical particles. Some of the spheres are filled with smaller spherical particles. Fig. 2(b) presents the SEM image of C-TiO₂/FAS, which confirms that C-TiO₂ was successfully coated on the FAS surface, consistent with the XRD results. However, due to the non-uniform shrinkage and fragmentation of the Ti gel in the drying and carbonization processes, the surface of C-TiO₂/FAS has a very uneven and rough appearance.

The nitrogen adsorption-desorption isotherms of the three samples were also measured and are shown in Fig. S2. The isotherms of the FAS, C-TiO₂, and C-TiO₂/FAS samples all show a typical type-IV behavior with a H3-type hysteresis loop, indicating the presence of uniform mesopores [28]. The pore sizes of the FAS, C-TiO₂, and C-TiO₂/FAS samples are 6.19, 11.67, and 12.61 nm, respectively. The BET surface area of C-TiO₂/FAS is 131.27 m² g⁻¹, which is ca. 20 times higher than that of the FAS sample (6.45 m² g⁻¹). Due to the relatively large specific surface area, C-TiO₂/FAS could provide a higher number of surface active sites.

3.2. Surface chemical analysis

XPS analyses were carried out to investigate the surface/interface chemical states of the samples. The overall XPS spectra of the FAS and C-TiO₂/FAS samples are shown in Fig. 3. Fig. 3(a) shows the XPS spectrum of FAS, which indicates that the FAS is mainly composed of Si, Al, O, and C elements [29]. Fig. 3(b) presents the XPS spectrum of the C-TiO₂/FAS sample. Compared to that in Fig. 3(a), the peak at a binding energy of 284 eV in Fig. 3(b), assigned to C-C neutral bonds [17], shows a clear increase, suggesting that the carbonization in N₂ atmosphere resulted in an increased amount of carbon species. In

Fig. 2. SEM images of (a) FAS and (b) C-TiO₂/FAS.

Fig. 3. XPS survey spectra of (a) FAS and (b) C-TiO₂/FAS; High-resolution (c) Si 2p and (d) Al 2p XPS spectra of FAS and C-TiO₂/FAS.

addition, a new Ti 2p peak located at 458.7 eV is observed in Fig. 3(b) [30], accompanied by a substantial decrease of the Si 2p and Al 2p peaks. This result provides further evidence that C-TiO₂ was successfully coated on the FAS surface, weakening the XPS signal of FAS. Fig. 3(c) and (d) show the Si 2p and Al 2p high-resolution XPS spectra of the FAS and C-TiO₂/FAS samples. The Si 2p peaks at 102.8 eV in Fig. 3(c) are ascribed to the Si 2p_{3/2} binding energy, indicating the presence of SiO₂ [31]. Moreover, the presence of α -Al₂O₃ in C-TiO₂/FAS and FAS is evidenced by the peak located at 74.2 eV in Fig. 3(d) [32]. The latter two figures also show a significant decrease in the intensity of the Al 2p and Si 2p peaks of C-TiO₂/FAS compared to those of the FAS sample, due to the coupling between C-TiO₂ and FAS.

Fig. 4 shows the C 1s, Ti 2p, and O 1s high-resolution XPS spectra of the C-TiO₂ and C-TiO₂/FAS samples, along with the ATR-FTIR spectra of the C-TiO₂, C-TiO₂/FAS, and FAS samples. As shown in Fig. 4(a), the C 1s spectra of C-TiO₂ and C-TiO₂/FAS can be deconvoluted into three peaks. The peaks at 284.5 eV can be ascribed to the C–C neutral bonds [17,18]. The peaks at 285.7–285.8 and 288.4–288.5 eV can be assigned to the

C–OR(H) and C–OOR(H) carbon species, respectively [16–19]. These results indicate that both samples were doped by the carbon species. The characteristic peak of O–Ti–C bonds (at 282.0 eV) is not present [16], indicating that the carbon dopants do not substitute the lattice oxygen of TiO₂.

To shed light on the chemical bond types at the surface/interface, ATR-FTIR spectroscopy was used to analyze the obtained samples. The peaks observed at ca. 1527 and 1445 cm^{−1} for C-TiO₂ and C-TiO₂/FAS in Fig. 4(b) can be attributed to the antisymmetric and symmetric stretching vibration of the bidentate carboxylate ligands on TiO₂; according to our previous results, these ligands derive from chelated acetic acid molecules (Fig. S3) [19]. It is worth noting that the intensity of the carboxylate peak is much lower for C-TiO₂/FAS than C-TiO₂, indicating that most of the bidentate carboxylate coordination has been destroyed by the coupling between C-TiO₂ and FAS. The peaks located at ca. 1411 cm^{−1} can be attributed the symmetric stretching vibration of carboxyl groups (–COOH) [33,34], while the shoulder peaks at ca. 1343 cm^{−1} are likely related to the deformation vibration of methyl groups (–CH₃) [33,35]. The peaks located at ca. 1050 and 1026 cm^{−1} for C-TiO₂

Fig. 4. (a) C 1s, (c) Ti 2p, and (d) O 1s high-resolution XPS spectra with constituent fitting and (b) ATR-FTIR spectra of C-TiO₂ and C-TiO₂/FAS.

are attributed to the stretching vibrations of C–O bonds of ring COH, COC, and CH₂OH groups [35–38], which is consistent with the C 1s XPS results. In the case of FAS, the peaks at ca. 1057 and 818 cm⁻¹ can be assigned to the asymmetric and symmetric stretching vibrations of Si–O–Si bridges [39,40], respectively. Upon coupling between C-TiO₂ and FAS, the peak at 818 cm⁻¹ disappears in C-TiO₂/FAS, and the intensity of the peak at 1057 cm⁻¹ markedly decreases. This result could be attributed to the coating of C-TiO₂ on the FAS surface, as revealed by the XRD, SEM, and XPS results. Furthermore, a new peak located at ca. 1090 cm⁻¹ is observed in C-TiO₂/FAS, which can be assigned to the asymmetric Si–O–C stretching mode [41,42]. Considering that the carbon species in FAS have been removed during the high-temperature pretreatment process, the formation of Si–O–C bonds should be related to the interaction between Si species of FAS and carbon dopants of C-TiO₂. In addition, upon coupling between C-TiO₂ and FAS, the stretching vibration of the Al–O bonds shifts from ca. 733 cm⁻¹ for FAS [40,43] to ca. 720 cm⁻¹ for C-TiO₂/FAS, which can be explained by the inductive effect caused by adjacent atoms or groups. Generally, a peak shift to lower wavenumbers is related to electron-donating groups, while the opposite is true for a shift to

higher wavenumbers [44,45]. The possible adjacent atoms and groups in the present study are represented by Ti atoms and methyl groups. Considering the negligible methyl content in C-TiO₂/FAS, it is reasonable to assume that the peak shift of the Al–O stretching vibration is caused by the formation of Al–O–Ti bonds. Therefore, it can be concluded that the coupling between C-TiO₂ and FAS results in the formation of Si–O–C and Al–O–Ti bonds at their interface, which consequently breaks the coordination of bidentate carboxylate ligands to TiO₂.

The high-resolution XPS spectra of the Ti 2p region are shown in Fig. 4(c). The peaks located at 458.0–458.7 and 463.8–463.9 eV correspond to the Ti 2p_{3/2} and Ti 2p_{1/2} binding energy regions, respectively [19,46]. In the case of C-TiO₂, a careful peak-fitting reveals that the Ti 2p_{3/2} peak can be further deconvoluted into two components at 458.0 and 458.7 eV, indicating two different types of electronic environments for Ti cations. Our previous studies demonstrated that the split of the Ti 2p_{3/2} peak can be attributed to the bidentate coordination of carboxylate ligands to Ti cations [19,47,48]. However, the carboxylate coordination peak disappears in C-TiO₂/FAS, suggesting that the coupling between C-TiO₂ and FAS with the formation of Si–O–C and Al–O–Ti bonds broke the coordination of

carboxylate ligands, as revealed by the ATR-FTIR results.

The above changes can also be observed in the O 1s high-resolution XPS spectra, shown in Fig. 4(d). The peaks at 529.4 eV are attributed to the O^{2-} anions in the TiO_2 lattice [19]. In the C- TiO_2 spectrum, the peak at 531.1 eV can be attributed to surface hydroxyl groups ($-OH$) or to $C=O$ groups from carbon dopants, whereas the peak at 532.5 eV can be assigned to bidentate carboxylate ligands, according to our previous results [19,47,48]. However, both peaks disappear in the spectrum of C- TiO_2 /FAS, and three new peaks are observed. Based on the ATR-FTIR results, the peak centered at 532.9 eV can be mainly ascribed to the SiO_2 component of FAS, rather than to bidentate carboxylate ligands [49,50]. The peak at 531.4 eV can be attributed to contributions from the surface hydroxyl groups [19], Al_2O_3 from FAS [51–53], and/or carbon dopants [17]. In particular, the peak centered at 530.5 eV, between the TiO_2 (529.4 eV) and Al_2O_3 (531.4 eV) peaks, can be attributed to the formation of Al–O–Ti bonds [53–55], confirming the results of the ATR-FTIR measurements. Based on the above analyses, we can conclude that the electronic environments of Ti, C cations and O anions were significantly affected by the coupling between C- TiO_2 and FAS and the subsequent formation of Si–O–C

and Al–O–Ti bonds. It can be expected that the electronic band structure of C- TiO_2 /FAS will also be different from that of C- TiO_2 .

3.3. Analysis of energy band structure

As shown in Fig. 5, the energy band structures of FAS, C- TiO_2 , and C- TiO_2 /FAS were analyzed in detail by UV-Vis DRS and valence band XPS (VB-XPS) [56,57]. Fig. 5(a) shows the UV-Vis DRS spectra of the three samples. Interestingly, the UV-Vis DRS spectrum of FAS shows semiconductor-like absorption. The maximum optical absorption threshold of FAS, as determined from Fig. 5(a), is located at ca. 445 nm, corresponding to a bandgap of 2.79 eV. For C- TiO_2 , the maximum optical absorption threshold is located at ca. 641 nm, corresponding to a bandgap energy of 1.93 eV. Compared to that of pure anatase TiO_2 , the absorption band edge of C- TiO_2 exhibits an evident red shift, revealing a substantial bandgap narrowing, which could be attributed to the carbon doping of TiO_2 [16–19]. Notably, upon coupling between C- TiO_2 and FAS, the absorption band edge of C- TiO_2 /FAS exhibits a remarkable blue shift compared to that of C- TiO_2 , indicating bandgap broadening.

Fig. 5. (a) UV-Vis DRS spectra of FAS, C- TiO_2 , and C- TiO_2 /FAS; valence band XPS spectra of (b) C- TiO_2 and (c) C- TiO_2 /FAS; (d) scheme of proposed energy band structure.

The maximum optical absorption threshold of C-TiO₂/FAS is located at ca. 515 nm, and the corresponding bandgap is 2.41 eV. According to the ATR-FTIR and XPS results, the bandgap broadening is likely related to the formation of Si–O–C and Al–O–Ti bonds at the interface between C-TiO₂ and FAS. In addition, the overall visible-light absorbances of C-TiO₂ and C-TiO₂/FAS are enhanced to various degrees compared to that of FAS, which could be attributed to the absorption arising from the carbon dopants on the surface of TiO₂ [16,19].

Figs. 5(b) and (c) show the valence band (VB) total density of states (DOS) of C-TiO₂ and C-TiO₂/FAS, respectively, measured by VB-XPS. The VB edges of C-TiO₂ and C-TiO₂/FAS are located at 1.87 and 2.23 eV, respectively. Therefore, the coupling between C-TiO₂ and FAS gives rise to a positive shift of the VB edge of C-TiO₂, denoting an enhanced oxidation capability of photogenerated holes. Moreover, both samples possess band tail states near their VB edges. For C-TiO₂, the band tail state can be attributed to the electron-withdrawing bidentate carboxylate ligands [19,47,48]. However, in the case of C-TiO₂/FAS, the band tail state is not expected to be related to the bidentate carboxylate ligands, because most of the bidentate carboxylate coordination has been destroyed by the coupling between C-TiO₂ and FAS. By combining the ATR-FTIR and XPS results, such band tail could be attributed to the Si–O–C and Al–O–Ti bonds at the interface between C-TiO₂ and FAS, which induce additional diffusive electronic states above the VB edge.

Fig. 5(d) shows schematic illustrations of the energy band structures of C-TiO₂ and C-TiO₂/FAS, constructed according to the UV-Vis DRS and VB-XPS data. The VB-XPS spectra of the samples show that the VB edges of C-TiO₂ and C-TiO₂/FAS are located at ca. 1.87 and 2.23 eV, respectively; at the same time, the UV-Vis DRS spectra reveal that the bandgaps of C-TiO₂ and C-TiO₂/FAS are ca. 1.93 and 2.41 eV, respectively. Therefore, the corresponding conduction band minimum (CBM) should be located at –0.06 eV for C-TiO₂ and –0.18 eV for C-TiO₂/FAS. Moreover, the presence of VB band tails can further shift the valence band maximum (VBM) energies up to ca. 1.26 eV for C-TiO₂ and 1.80 eV for C-TiO₂/FAS. Consequently, a marked bandgap narrowing is observed in C-TiO₂ (1.32 eV) and C-TiO₂/FAS (1.98 eV), caused by the VB tail states. Therefore, it can be concluded that the coupling between C-TiO₂ and FAS and the formation of Si–O–C and Al–O–Ti bonds could not only induce a positive shift of the VB edge, but also further narrow the bandgap of C-TiO₂/FAS via the VB tail states.

3.4. Recombination of photogenerated carriers

PL emission spectra have often been employed for understanding photocatalytic surface processes by characterizing the separation efficiency of photogenerated charge carriers, because the PL emission mainly arises from the recombination of photogenerated electrons and holes [58]. The PL spectra of the different samples were measured with an excitation wavelength of 450 nm under room conditions and are shown in Fig. 6. The PL peak intensity of FAS is significantly stronger than that of the other two samples. Because the main components of

Fig. 6. Photoluminescence spectra of different samples with an excitation wavelength of 450 nm.

FAS are SiO₂ and Al₂O₃, FAS should be regarded as an insulating material. Hence, the exact reason for the formation of the PL emission in FAS remains unknown. A possible source of PL emission might be the presence of trace amounts of ferric and/or titanium oxides in FAS, which leads to the absorption of visible-light and the generation and recombination of charge carriers, as revealed by the UV-Vis DRS results. The PL peak intensity of C-TiO₂/FAS is very close to that of C-TiO₂, and much lower than that of FAS. The relatively low PL peak intensity of C-TiO₂/FAS indicates that the recombination process of photo-generated charge carriers was effectively inhibited.

Time-resolved fluorescence measurements can provide more information about the dynamics of charge separation compared to steady-state ones; therefore, we carried out time-resolved photoluminescence experiments with an excitation wavelength of 350 nm [59]. As shown in Fig. S4, all three samples exhibit a typical single-exponential decay. The fluorescence lifetimes of the FAS, C-TiO₂, and C-TiO₂/FAS samples are 0.64, 0.61, and 0.64 ns, respectively. This result indicates that the coupling between C-TiO₂ and FAS promotes the separation of carriers.

3.5. Photocatalytic activity

The photocatalytic activity of the different samples was evaluated by monitoring the photocatalytic degradation of an aqueous solution of MO, as shown in Fig. 7. The adsorption-desorption equilibrium of MO in a dark environment is achieved within 60 min. In this stage, C-TiO₂ and C-TiO₂/FAS show a certain degree of adsorption of MO in water. To determine the potential adsorption of MO on FAS, static adsorption tests of MO on FAS were carried out in a dark environment. The results reveal that FAS does not show any appreciable adsorption of MO (Fig. S5). In the subsequent photodegradation process, C-TiO₂/FAS shows the highest photocatalytic activity among the three samples. Under 450 nm visible light irradiation, approximately 99% of MO (with an initial concentration of

Fig. 7. (a) Photocatalytic degradation of methyl orange (MO) in the presence of FAS, C-TiO₂, and C-TiO₂/FAS under visible light irradiation ($\lambda \geq 420$ nm); (b) Representative UV-Vis absorbance spectra of MO in water as a function of reaction time, using C-TiO₂/FAS as the photocatalyst; (c) Plot of $\ln C_0/C$ vs. irradiation time for C-TiO₂ and C-TiO₂/FAS, showing the corresponding rate constants; (d) Recycling properties of C-TiO₂/FAS in the photocatalytic degradation of MO.

20 mg/L) is degraded in 90 min using C-TiO₂/FAS as the photocatalyst. After irradiation for 90 min under the same conditions, the MO photodegradation efficiencies over FAS and C-TiO₂ are approximately 2.0% and 97.0%, respectively. Previous studies showed that carbon doping could effectively narrow the bandgap of TiO₂ and substantially improve the visible-light photocatalytic activity, resulting in the higher activity of C-TiO₂ [17,19,47,48]. The degradation of MO using uncoated FAS shows no obvious decrease in MO concentration, confirming that the fresh substrate has no photocatalytic activity. In the case of the photodegradation of MO on C-TiO₂/FAS, the representative UV-Vis absorbance spectra were also recorded as a function of reaction time (Fig. 7(b)). Photocatalytic degradation processes are often modeled as first-order kinetic processes. Fig. 7(c) shows the degradation kinetics results in the presence of C-TiO₂/FAS and C-TiO₂, revealing a linear relationship between $\ln(C_0/C)$ and the irradiation time t , which indicates that the photocatalytic degradation of MO follows a pseudo-first order kinetics: $\ln(C_0/C) = kt$, where C_0 is the initial MO concentration, C is the MO concentration at different irradiation times, and k is the pseudo-first order rate constant (min⁻¹). The cal-

culated k value for C-TiO₂/FAS (0.058 min⁻¹) is 1.76 times higher than that of C-TiO₂ (0.033 min⁻¹). As mentioned above, FAS has no photocatalytic activity on its own. However, the presence of FAS in the C-TiO₂/FAS composite played an important role in improving the MO photodegradation efficiency of C-TiO₂. This result may be rationalized by considering that the coupling between C-TiO₂ and FAS and the subsequent formation of Si-O-C and Al-O-Ti bonds at their interface lead to a positive shift of the VB edge of C-TiO₂, enhancing its oxidation ability of photogenerated holes as well as its MO photodegradation efficiency.

Reusing experiments were also performed to evaluate the photostability of C-TiO₂/FAS. Fig. 7(d) shows the results of six successive MO photodegradation runs under the same experimental conditions. The catalytic activity of the C-TiO₂/FAS sample shows a slight decrease but remains higher than 85% after each cycle, demonstrating the good reusability of the catalyst for the photodegradation of MO. Compared to unsupported C-TiO₂, the C-TiO₂/FAS composite exhibits much better settleability (Fig. S6). Therefore, the C-TiO₂/FAS composite can be easily separated from the reaction system.

Fig. 8. (a) Effects of different scavengers on the degradation of MO in the presence of C-TiO₂/FAS; (b) Schematic illustration of the proposed band structure of C-TiO₂/FAS and of the visible-light photocatalytic process.

To further investigate the photocatalytic mechanism of the C-TiO₂/FAS composite, the oxidative species in the photocatalytic degradation process were identified through radical- and hole-trapping experiments. As shown in Fig. 8(a), the photocatalytic degradation of MO was markedly inhibited by the addition of both triethanolamine (hole scavenger) [60] and *p*-benzoquinone (superoxide radical scavenger) [61]. This result indicates that both holes and superoxide radicals play important roles in the photocatalytic degradation of MO. A possible photocatalytic mechanism of C-TiO₂/FAS, based on the characterization results described above, is presented in Fig. 8(b). Upon visible-light irradiation, electrons are excited directly into the C-TiO₂/FAS conduction band and transferred to adsorbed oxygen molecules to produce $\cdot O_2^-$ species and subsequently the strongly oxidizing $\cdot OH$ radicals. At the same time, the photogenerated holes will oxidize adsorbed water molecules to produce $\cdot OH$ radicals. The adsorbed MO molecules can thus be attacked by the $\cdot OH$ radicals.

4. Conclusions

A C-TiO₂/FAS composite photocatalyst was successfully synthesized using a sol impregnation and carbonization method. The carbon dopants were derived from the organic species generated during the synthesis of C-TiO₂/FAS. The coupling between C-TiO₂ and FAS resulted in the formation of Si–O–C and Al–O–Ti bonds at the interface, which broke the coordination of bidentate carboxylate ligands to TiO₂. The presence of Si–O–C and Al–O–Ti bonds gave rise to a positive shift of the VB edge of C-TiO₂, enhancing its oxidation ability of photogenerated holes as well as its MO photodegradation efficiency. In addition, the C-TiO₂/FAS photocatalyst exhibited good reusability and separability. This work may provide a new route for tuning the electronic band structure of TiO₂.

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Graphical Abstract

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Enhanced visible-light photocatalytic oxidation capability of carbon-doped TiO₂ via coupling with fly ash

Ning An, Yuwei Ma, Juming Liu *, Huiyan Ma, Jucai Yang, Qiancheng Zhang *

Inner Mongolia University of Technology; University of Science and Technology Beijing

The coupling between C-TiO₂ and FAS led to a positive shift of the valence band edge of C-TiO₂, enhancing its oxidation capability of photogenerated holes and improving its methyl orange photodegradation efficiency.

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与粉煤灰耦合增强碳掺杂TiO₂的可见光催化氧化能力

安 宁^a, 马雨威^b, 刘聚明^{a,*}, 马惠言^a, 杨桔材^c, 张前程^{a,#}

^a内蒙古工业大学化工学院, 内蒙古自治区工业催化重点实验室, 内蒙古呼和浩特010051

^b北京科技大学材料科学与工程学院, 北京100083

^c内蒙古工业大学能源与动力工程学院, 内蒙古呼和浩特010051

摘要: 半导体光催化技术是利用太阳能消除有机污染物的最佳解决方案之一。二氧化钛(TiO₂)是在该领域应用最广泛的光催化剂, 具有无毒、廉价、抗光腐蚀等优异性能。然而, 纯TiO₂在可见光下的光催化活性较差, 这限制了TiO₂光催化技术的进一步发展和实际应用。对此, 学者们进行了多方面研究来拓展TiO₂对可见光的吸收范围并提升其光催化活性。研究表明, 对TiO₂进行碳掺杂是拓展其光吸收范围和增强其可见光催化活性的有效方法。

粉煤灰是燃煤电厂原煤燃烧产生的一种固体废物。粉煤灰的随意堆积和不适当处置可导致土壤、空气、水甚至生态系统的严重污染。因此, 粉煤灰的回收利用引起了许多研究者的关注。事实上, 粉煤灰有其自身独特的优点, 如无毒、低成本和化学/物理稳定性等。这些性质使得粉煤灰可以作为一种很有前景的催化剂载体材料。最近, 很多学者以粉煤灰为载体合成了多种TiO₂/粉煤灰复合光催化剂, 并对所制备催化剂的结构、性质及其光催化性能进行了研究。但是, 将碳掺杂TiO₂与粉煤灰进行耦合的研究一直未见报道, 而且关于粉煤灰载体对TiO₂光催化活性的促进机理, 特别是粉煤灰负载对TiO₂能带结构及其光催化活性的影响仍缺乏深入和系统的研究。

本文采用简单的溶胶浸渍+炭化的方法制备了碳掺杂TiO₂/粉煤灰载体(C-TiO₂/FAS)复合光催化剂。其中的碳掺杂组分源于合成过程中加入的有机成分(钛酸四丁酯、乙酸和乙醇), 在负载及炭化过程中这些有机组分同步进入TiO₂体相及表面形成碳掺杂。采用多种表征方法对所制备的光催化剂进行了表征。XRD, SEM和XPS表征结果表明, C-TiO₂组分很好地包覆在粉煤灰球形颗粒表面。XPS和ATR-FTIR表征结果表明, 随着C-TiO₂与FAS的耦合, C-TiO₂表面原有的羧基螯合结构被破坏, 并在其界面上形成了Si-O-C和Al-O-Ti键。UV-Vis DRS和VB-XPS表征结果表明, 碳掺杂缩减了TiO₂的禁带宽度, 显著拓展了光吸收范围。Si-O-C和Al-O-Ti键的存在引起了C-TiO₂价带边的正向移动, 意味着光生空穴氧化能力增强。稳态PL及时间分辨PL表征结果表明, C-TiO₂/FAS光生载流子的复合率较低。在可见光催化活性测试中, C-TiO₂/FAS对甲基橙显示出较高的光催化降解效率, 这主要是由于C-TiO₂/FAS较低的价带位置增强了光生空穴的氧化能力, 进而提高了催化剂对甲基橙的降解效率。自由基捕获实验结果表明, 在降解过程中光生空穴及超氧自由基是关键活性物种。此外, C-TiO₂/FAS可以很方便地通过自然沉降进行固液分离, 并表现出很好的重复利用降解活性。

关键词: 粉煤灰; 二氧化钛; 碳掺杂; 可见光催化; 光催化氧化

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*通讯联系人. 电子信箱: liujuming@imut.edu.cn

#通讯联系人. 电子信箱: jzhang@imut.edu.cn

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