

Preparation and photocatalytic activity of nano-TiO₂ codoped with fluorine and ferric

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Abstract: Nano-F⁻/Fe³⁺/TiO₂ particles were prepared by hydrolysis of tetrabutyl titanate in a mixed CF₃COOH-Fe(NO₃)₃-H₂O solution. The photocatalytic decomposition of methylene blue in aqueous solution was used as a probe to evaluate their photocatalytic activities. The powders were characterized by X-ray diffraction (XRD), energy dispersion X-ray spectrum (EDS) and Brunauer-Emmett-Teller (BET) surface area analysis. The results show that F⁻ and Fe³⁺ are doped into TiO₂. The F⁻ and Fe³⁺ doping can help to enhance the nano-TiO₂ photocatalytic activity greatly. The appropriate codoping conditions for F-Fe are $n(\text{F})/n(\text{TiO}_2)=2\%$, $n(\text{Fe})/n(\text{TiO}_2)=0.05\%$, and the degradation rate of methylene blue at 1 h is improved from 73.2% to 87.5%. The codoped nano-F⁻/Fe³⁺/TiO₂ particles have higher BET specific surface area, smaller crystallite size and higher photocatalytic activity than those of undoped TiO₂ particles.

Key words: nano-TiO₂; F⁻/Fe³⁺/TiO₂; codoping; photocatalytic activity

1 Introduction

Titanium dioxide is widely used as a photocatalyst because of its photochemical stability, non-toxicity and low-cost[1]. However, the low efficiency for the utilization of visible light and recombination between the photogenerated electrons and holes are often two major limiting factors that impede the enhancement of photocatalytic activity. Many studies have been devoted to the improvement of photocatalytic efficiency of TiO₂, such as doping metal or non-metal ions[2–4], depositing noble metals[5–6], surface sensitization[7] and composite semiconductor[8–9].

Doping transition metals or non-metal ions are effective method to improve photocatalytic activity of nano-TiO₂. XIN et al[10] revealed the mechanisms of photoinduced carriers separation and recombination of Fe³⁺-TiO₂ photocatalysts, that is, Fe³⁺ captured the photoinduced electrons, inhibiting the recombination of

photoinduced electron-hole pairs. YU et al[11] prepared F⁻-doped TiO₂ powders by hydrolysis of titanium tetraisopropoxide in a mixed NH₄F-H₂O solution and found that photocatalytic activity of F⁻-doped TiO₂ powders exceeded that of Degussa P25 when the molar ratio of NH₄F to H₂O was kept in the range of 0.5–3.0.

In this work, F⁻ and Fe³⁺-codoped TiO₂ nanoparticles were prepared from tetrabutyl titanate through sol-gel method, characterized by means of X-ray diffraction (XRD), energy dispersion X-ray spectrum (EDS) and Brunauer-Emmett-Teller (BET) surface area analysis. The photocatalytic activities of the prepared powders were studied following the degradation of methylene blue.

2 Experimental

2.1 Preparation of F⁻-Fe³⁺-TiO₂ nanoparticles

Specimens of F⁻-Fe³⁺-TiO₂ containing different amounts of F⁻ and Fe³⁺ were prepared by sol-gel method.

10 mL of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was added slowly into mixed solution containing 15 mL $\text{C}_2\text{H}_5\text{OH}$ and 4.5 mL CH_3COOH to form solution A. Meanwhile CF_3COOH and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added into mixed solution containing 4 mL water, 7.5 mL $\text{C}_2\text{H}_5\text{OH}$ and 4.5 mL CH_3COOH to form solution B. Then the solution B was added dropwise into the solution A under vigorous stirring at room temperature. The resulting transparent colloidal liquid was continuously stirred till the gel was formed. The gel was dried at 110°C for 6 h, calcined at 450°C for 2 h in air and ground to obtain the F^- - Fe^{3+} - TiO_2 nanoparticles. The molar ratios of F to Ti are 0 and 2%, and the molar ratios of Fe^{3+} to Ti are 0, 0.01%, 0.03%, 0.05%, 0.1% and 0.15%.

2.2 Characterization of samples

The XRD patterns obtained on a BRUKER D8-ADVANCE X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda=0.1542\text{ nm}$) at a scan rate of $0.05^\circ/\text{s}$ were used to determine the crystal structure and crystallite size. The accelerating voltage and the applied current were 15 kV and 20 mA, respectively. The crystallite size of the anatase was determined by applying Scherrer equation to XRD data. Energy dispersive X-ray spectroscopy (EDS) was recorded on a PHILIP XL-30 ESEM. The BET surface area was determined using a specific surface area analysis meter (Quantachrome NOVA2000).

2.3 Photocatalytic activity measurement

The photocatalytic degradation of methylene blue over photocatalysts was carried out in XPA-II photochemical reactor (Nanjing Xujiang Electromechanical Factory). A 500 W high-pressure mercury lamp was used as light source, whose photo intensity was $0.22\text{ kW}\cdot\text{m}^{-2}$ at 365 nm. In each run, 0.05 g photocatalysts were added into 100 mL methylene blue solution of $13\text{ mg}\cdot\text{L}^{-1}$. After premixing for 5 min, the light was turned on to initiate the reaction for 1 h. A 723 spectrometer was used to determine the concentration of methylene blue solution before and after photocatalytic degradation.

3 Results and discussion

3.1 EDS spectrum

The EDS spectrum of the F^- - Fe^{3+} - TiO_2 sample with molar ratios of F and Fe to Ti of 2% and 0.05% is shown in Fig.1. The EDS spectrum indicates that there are F and Fe elements in the sample, that is, F^- and Fe^{3+} can be doped into TiO_2 through hydrolysis of tetrabutyl titanate by using CF_3COOH and $\text{Fe}(\text{NO}_3)_3$ as dopant.

3.2 XRD and BET analysis

Fig.2 shows the XRD patterns of TiO_2 and

F^- - Fe^{3+} - TiO_2 sample, in which molar ratios of F and Fe to Ti are 2% and 0.05%. It can be seen that the diffraction peaks of samples are all ascribed to the anatase phase.

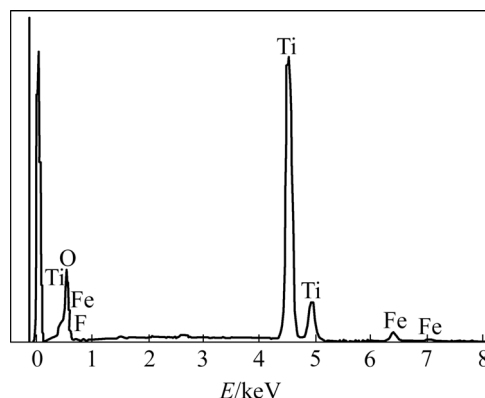


Fig.1 EDS spectrum of $\text{F}^-/\text{Fe}^{3+}/\text{TiO}_2$

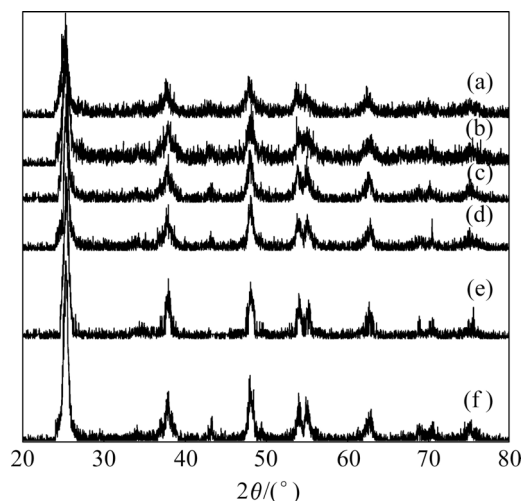


Fig.2 XRD patterns of TiO_2 and F^- - Fe^{3+} - TiO_2 powders calcined at 450°C for 2 h: (a) 2%F-0.15%Fe- TiO_2 ; (b) 2%F-0.10%Fe- TiO_2 ; (c) 2%F-0.05%Fe- TiO_2 ; (d) 2%F-0.03%Fe- TiO_2 ; (e) 2%F-0.01%Fe- TiO_2 ; (f) TiO_2

With the increase of Fe-doping concentration, the peak intensities of anatase slightly decrease and the width of plane diffraction peak becomes broader. Therefore, it is reasonable to deduce that the larger the amount of Fe-doping, the poorer the crystallization of the TiO_2 powders and the smaller the crystallite size of TiO_2 . The results are the same as those of the BET surface area analysis shown in Table 1. It can be seen that the codoping of F^- and Fe^{3+} can inhibit the growth of TiO_2 crystal.

3.3 Evaluation of photocatalytic activity

Table 2 lists the photocatalytic degradation rate of methylene blue over F^- - Fe^{3+} - TiO_2 photocatalysts with $n(\text{F})/n(\text{Ti})$ of 2% and different Fe^{3+} dopant contents. F^- -doping can convert some Ti^{4+} to Ti^{3+} by charge

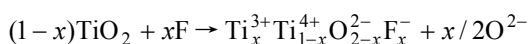
Table 1 Effects of Fe-doping concentration on physical properties of TiO₂ powders with $n(\text{F})/n(\text{TiO}_2)$ of 2%

Sample	Crystalline size/nm	Surface area/(m ² ·g ⁻¹)
TiO ₂	15.8	92.3
2%F-0.01%Fe-TiO ₂	15.0	98.5
2%F-0.03%Fe-TiO ₂	13.8	110.3
2%F-0.05%Fe-TiO ₂	11.9	123.5
2%F-0.10%Fe-TiO ₂	10.7	130.6
2%F-0.15%Fe-TiO ₂	10.1	138.5

Table 2 Degradation ratio of methylene blue by codoped TiO₂ with different concentrations of F⁻ and Fe³⁺

$n(\text{F})/n(\text{Ti})/\%$	$n(\text{Fe})/n(\text{Ti})/\%$	Degradation ratio of methylene blue/%
0	0	73.2
2	0.01	76.1
2	0.03	84.7
2	0.05	87.5
2	0.1	82.2
2	0.15	75.3

compensation[11–12]:



Since TiO₂ is an n-type semiconductor, Ti³⁺ in TiO₂ forms a donor level between the band gaps of TiO₂. Ti³⁺ may trap the photogenerated electrons and then reduce recombination rate of electrons and holes and enhances photocatalytic activity. In the work, the molar ratio of F to Ti is fixed at 2%.

It can also be found that the photodegradation ratio of methylene blue increases with the increase of content of Fe³⁺ dopant. When the content of Fe³⁺-TiO₂ is over 0.05%(molar fraction), the degradation ratio of methylene blue is the highest, which can be attributed to the following reasons. Appropriate amount of the doped Fe³⁺ ($\leq 0.05\%$) in TiO₂ can effectively capture the photoinduced electrons, which inhibits the holes-electrons recombination and induces more photo-generated electrons and holes to participate in the photocatalytic reactions. When the content of Fe³⁺ dopant exceeds 0.05%(atom fraction), it can be seen that the degradation ratio decreases. The reason is that the photocatalytic activity of Fe-doped TiO₂ is strongly dependent on the dopant concentration since Fe³⁺ can serve as not only a mediator of interfacial charge transfer but also a recombination center[10, 13]. In this case, an optimal dopant concentration is 0.05%(molar fraction). Above that concentration, Fe³⁺ steadily becomes recombination center of the photoinduced electrons and holes, which is unfavorable to photocatalytic reactions.

4 Conclusions

1) Nano-F⁻/Fe³⁺/TiO₂ particles are prepared by hydrolysis of tetrabutyl titanate in a mixed CF₃COOH-Fe(NO₃)₃-H₂O solution. The EDS spectrum indicates that there are F and Fe elements in the sample.

2) At an optimal concentration of $n(\text{Fe})/n(\text{Ti})=0.05\%$ and $n(\text{F})/n(\text{Ti})=2\%$, the photocatalytic activity of F⁻-Fe³⁺-TiO₂ powders prepared by this method and calcined at 450 °C shows the highest activity. The degradation rate of methylene blue at 1 h is improved from 73.2% to 87.5%.

3) The codoping of F⁻ and Fe³⁺ can inhibit the growth of TiO₂ crystal. Nano-F⁻/Fe³⁺/TiO₂ particles have higher BET specific surface area and smaller crystallite size than those of undoped TiO₂ particles.

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