

Preparation, Microstructure and Performance of Activated FA / TiO₂-WO₃ Composite Photocatalyst

Abstract: In this work, the fly ash(FA) carrier surface was activated and modified by sulfuric acid and tetrabutyl titanate sol, the TiO₂-WO₃/FA composite photocatalyst were prepared by a simple wet-chemical method. The phase, composition and surface microstructure were investigated by XRD, SEM and EDS. On that basis, the photocatalytic activity of composite photocatalyst was researched in the methyl orange dye. The results showed that the activated FA increased specific surface area by H₂SO₄ soaking and the modified FA was more beneficial to loading photocatalysts via tetrabutyl titanate sol processing. The as-prepared TiO₂-WO₃ FA composite photocatalyst showed the higher photocatalytic degradation efficiency under UV irradiation, the composite photocatalyst decolorization efficiency with wt5% loading amount can reach 97% after 30 min. Meanwhile, the mechanism of action and carrier effect were discussed.

Key words: FA; TiO₂-WO₃; composite photocatalyst; microstructure

1. Introduction

In recent years, the no application of the semiconductor photocatalysis for remedying the problem of chemical wastes in water has attracted much attention. In the most of semiconductor photocatalysts, the TiO₂ is considered as the most promising photocatalyst due to its excellent functionality, stability, low-cost and nontoxicity. However, in practical application, the nano-TiO₂ powder has a large band gap and it absorbs only a small portion of near ultraviolet region solar light [1-2]. Meanwhile, difficult to recycle, not suitable for flowing system. Therefore, on the one hand, many attempts have been devoted to improving the activity of TiO₂ and its photocatalytic efficiency under visible light, such as compound, doping ions, supported expensive metals and outfield assistant and so on [3-5]. On the other hand, the photocatalyst fixation is also a major research field.

FA as the solid by-product of coal-fired power plants was recognized to pose huge environmental problems, therefore, more and more research are devoted to identifying various effective paths to use the ash [6-7]. Among them, FA particles as a novel type of photocatalyst carrier represent a highly promising alternative due to their high chemical stability, high surface area and high adsorption capacity. However, the FA particles surface were wrapped by the stability glass shell, its potential activity was influenced [8]. So, how to modify and activate the potential activity of FA, as a novel photocatalyst carrier, it has important practical significance to improve the added value and comprehensive utilization of FA [9].

In this work, the FA was first modified by acid dissolution method, then, its surface was treated with butyl titanate sol, the modified FA was used as carrier for the immobilization of industrial nano-TiO₂-WO₃ composite photocatalyst. The photocatalytic activity was investigated in the methyl orange dye and clarified based on X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), scanning electron microscopy (SEM). The influence of key operational parameters, such as the phase, composition, surface microstructure has been as well considered.

2. Experimental

2.1 Reagent and Instrument

All chemicals were of reagent grade and were used without further purification. The FA was collected

from the electro-filters of the thermal power plant in Hebei Province Baoding City(China).The $\text{TiO}_2\text{-WO}_3$ (WO_3 wt 3%), powder were commercial product purchased from Jiangsu Catalyst Co., Ltd.

The surface microstructure and surface elements of samples were characterized by using SEM(JSM-7500F, JEOL), XRD (Y2000) and EDS (NAROUSA). Analysis of the as-prepared photocatalysts was carried out at room temperature with a Y-2000 apparatus using Cu target(Dandong ray instrument Co., Ltd.China).The BET surface area were determined using a Micromeritics Tristar II 3020 surface area and pore analyzer(Micromeritics, USA).The UV-Vis absorption spectra of samples was observed by TU-1900 UV-Vis spectrophotometer.

2.2 Activation and surface modification of FA

The acid activation of FA was conducted by mixing the ash with a 1M H_2SO_4 dissolution, the solution was under vigorous stirring for 4h at 40 °C, then, the wet FA was filtered, washed and dried. In order to obtain improved interaction between FA and photocatalyst, according to the literature, the surface modification of FA was conducted by tetrabutyl titanate-ethanol-triethanolamine sol system. The acid activated FA was added to the configured sol for 2h under magnetic stirring and aged 24 h. The suspension was afterwards filtered, the obtained product is surface modified FA.

2.3 Preparation of nano- $\text{TiO}_2\text{-WO}_3$ /FA composites photocatalyst

The nano- $\text{TiO}_2\text{-WO}_3$ powder was mixed with 10ml ethanol under an ultrasonic system for 1h, then, the activated and modified FA was added to this solution and for the mixture was stirred for a further 2 h. The product was filtered and dried, finally, the samples were calcined in the muffle furnace at 450 °C for 4 h. The $\text{TiO}_2\text{-WO}_3$ /FA composite photocatalyst were prepared in the same way, the different weight rate photocatalyst were also as-prepared via the same method.

2.4 Photocatalytic activity test

The light source was provided by a 40W ultraviolet light lamps (wavelength 2537 Å), which were placed above the reactor for 6cm, methyl orange dye was used as a target reactant. The photocatalysts were added into 50 mL methyl orange solution (20 mg/L) under the magnetic stirring in the photochemical reactor, after irradiation under different time period, by the way of taking the supernatant liquor, centrifuged and filtrated, the photocatalytic activity was tested by UV-vis spectrophotometer at 465 nm. The photocatalytic degradation rate (D) was calculated by the following formula: $D = (A_0 - A) / A_0 \times 100\%$, where A_0 and A denote the absorbance of the dye solution before and after photocatalytic treatment respectively.

3. Results and discussion

3.1 XRD analysis

The phase structure and crystal form of different as-prepared samples are performed by X-ray diffraction. Fig. 1 shows the XRD patterns of the raw FA, activated and modified FA and composite photocatalysts. The phase composition of activated and modified FA (Fig. 1b) had not greatly change compared with the raw FA (Fig 1a). The typical diffraction peaks of quartz, mullite are evidenced in the patterns at 16.39 °, 26.01 °, 26.27 °, 33.23 °, 26.58 °, 20.86 ° ($\text{Al}_6\text{Si}_2\text{O}_{13}$:15-0776; SiO_2 :46-1045). Fig 1c shows the XRD pattern of composite photocatalyst. It can be seen that the new diffraction peaks at $2\theta=25.80$, 48.04 and 55.07 are clearly appeared, which can be assigned to the anatase TiO_2 (21-1272) and WO_3 (20-1324) respectively. It is mainly due to the photocatalyst($\text{TiO}_2\text{-WO}_3$) onto the FA surface. In addition, the photocatalyst after the photocatalytic process were comparatively investigated (Fig

1d). Compared with Fig 1c, the XRD spectra showed without significant changing, the composite photocatalyst was confirmed stability.

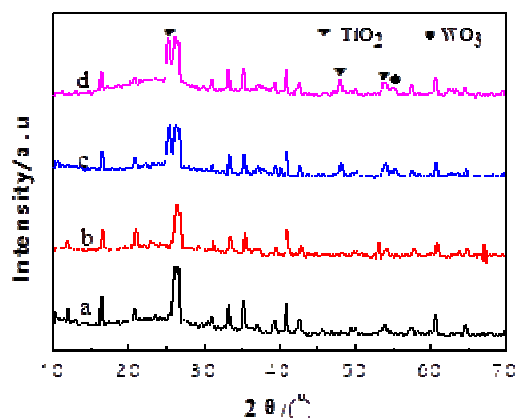


Fig.1 XRD spectra of samples

a:Raw FA; b: Activated modified FA; c:composite photocatalyst ; d:After photocatalysis

In order to investigate the effect of H_2SO_4 activated FA, the BET surface area was measured, the result showed that the specific surface area of activation FA was $15.5m^2/g$, which is larger than that of raw FA ($8.2m^2/g$). The reason may be H_2SO_4 activation altered the surface structure and composition of FA. In soaking process, the soluble alkaline oxides (K_2O , Na_2O , MgO , CaO) and free inorganic component were removed from the raw FA into the solution, the higher roughness and pores were re-formed in acid, resulting in the observed higher specific surface area.

3.2 SEM and EDS analysis

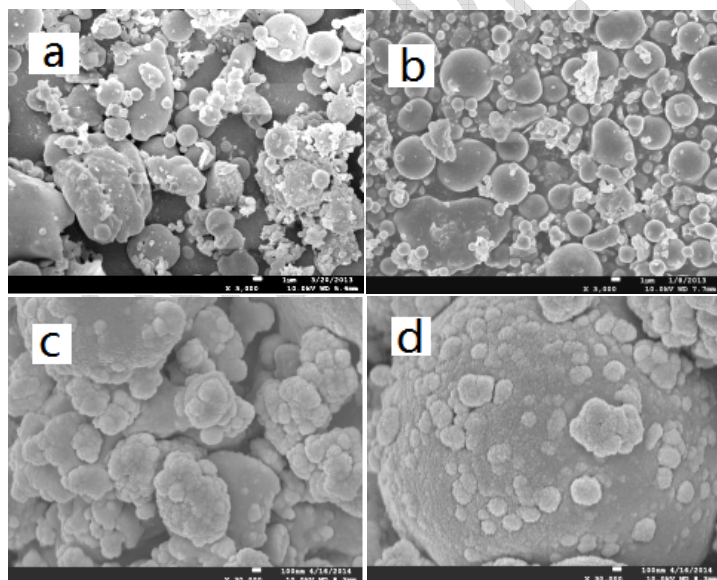


Fig.2 SEM photos

a:the raw FA; b:the sulfuric acid activated FA; c:FA/TiO₂-WO₃ before illumination; d: FA/TiO₂-WO₃

after illumination

The surface morphologies of as-prepared samples were investigated by SEM. The raw FA morphology was shown in Fig. 2a, as can be observed in Fig. 2a, the raw FA presents large particle aggregates with spherical and amorphous particle, the small glass beads were adhered to big particle surface. The activated FA image was shown in Fig. 2b, it can be clearly observed that the spherical particle was dispersion with a smooth surface. Fig. 2c,d show the surface morphology of composite photocatalyst before and after photocatalysis process, from Fig. 2c, we can see that the surface of FA became rougher, which indicates some nano-TiO₂-WO₃ particles coating on the surface, the catalysts size was about 20-30 nm. In Fig. 2d, after photo degradation process, a certain amount of photocatalyst particles was maintained on the FA surface, the stability and activity of composite photocatalyst were proved.

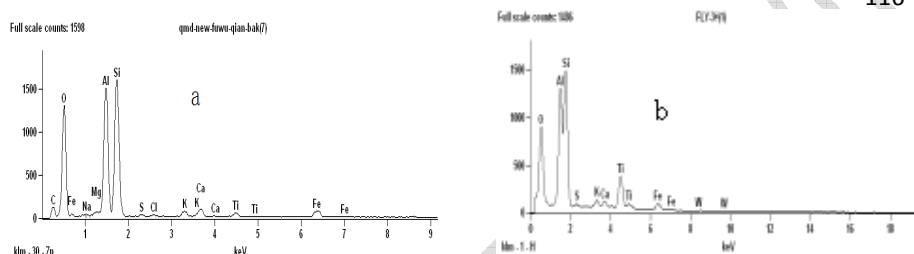


Fig.3 EDS spectrums of FA

a:raw FA; b:sinking beads

The chemical constituents of samples were revealed by EDS analysis. The typical spectra were shown in Fig. 3. The result show that raw FA mainly consisted of Si, Al, and O elements, and small amounts of elements such as Ca, Ti, Fe, Mg, etc. (Fig. 3a), compare with Fig. 3b, it can be clearly seen increasing Ti, W element peak in the composite photocatalyst. The combined results of SEM, it was further confirmed that the photocatalyst was well-loaded on the FA particles surface by activation and modifier process.

3.3 Photocatalytic activity studies

In order to evaluate photocatalytic activity of composite photocatalyst, the photocatalytic degradation of MO (20 mg/L) was carried out under 40 W UV light irradiation [10]. The condition was fixed with the 50 mL MO solution, 200 mg composite photocatalyst and 30 min time. The Fig. 4 shows the photocatalytic activity at the different TiO₂-WO₃ loading capacity of composite photocatalyst. It can be seen that the TiO₂-WO₃ loading capacity has a great influence on the photocatalytic decolorization performance. It may be noted that the decolorization efficiency is about 58%, when have not TiO₂-WO₃ composite photocatalyst. The reason was attributed to excitation and modify FA by H₂SO₄ and titanium sol, the decolorization ratio is mainly in connection with adsorption of FA and a small amount of TiO₂ film photocatalysis process with the surface of FA was modified by titanium sol [11]. With the increasing of the TiO₂-WO₃ loading amount in the range wt0.5%-5%, the decolorization efficiency increases from 76% to 97% after 90 min. However, further increasing the catalyst dosage from wt6%-10% resulting in a slight decrease in the decolorization efficiency. The reason may be a more photocatalyst suspension may lead to decrease of its transparency resulting in less efficient radiation penetration [12]. In order to further

investigate the decolorization efficiency, the wt0.5% (TiO₂-WO₃/FA) composite photocatalyst was used to compare with raw FA, activated FA and modified FA at different photocatalytic degradation time. The experimental results were shown in Fig.5, under the same condition, the decolorization rate of activation FA exhibit higher decolorization than raw FA in the first 10min. The decolorization rate was about 35% and 42% respectively, with the increase of time, the decolorization rate was stable, it was inferred that the adsorption process played a dominant role and reach adsorption-desorption equilibrium in 10 min. This results show that the adsorptive property of activation FA possess have good discoloring performance than raw FA due to the higher specific surface area. Compared with the modify FA by tetrabutyl titanate sol, the degradation and discoloring rate can reach about 50% in 10min, afterward, the discoloring rate emerge slowly increase with time increasing. The reason for the result was that the anatase TiO₂ film supported on FA surface, the photocatalytic degradation play its role effectively after adsorption equilibrium. In addition, it's worth noting that the highest degradation activity was shown in Fig.5. A significant increase in photocatalytic activity is exhibited by the as-prepared composite photocatalyst, the degradation and discoloring rate reach over 80% in 10min, the decolorization rate appeared gradually increasing with time extension and reached more than 97% at 90min under UV radiation. The results indicate that the as-prepared composite photocatalyst displayed excellent photocatalytic performance. The reason may be attributed to the doping WO₃ presence in composite photocatalyst. The TiO₂ and WO₃ simultaneously occur interband transitions under the UV irradiation [13]. The photoinduced electron transfer from the TiO₂ surface to the lower energy level WO₃ due to different energy levels, the WO₃ induced hole was migrated to the higher TiO₂ valence band, this process suppressed the electron-hole pair recombination [14-16]. On the other hand, the photocatalytic process was mainly carried out on the catalyst surface, a larger specific surface area FA carrier had been confirmed by activating and modifying process, meanwhile some elements (Fe, S, etc) of FA carrier may be enhanced photocatalytic activity due to improve the absorption threshold and reduce the hole-electron pair recombination. So, the as-prepared composite photocatalyst showed the higher photocatalytic degradation efficiency.

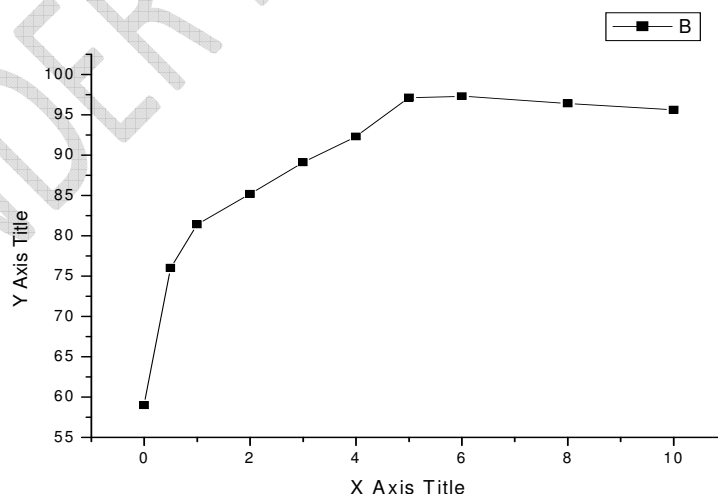


Fig.4 Effect of TiO₂-WO₃ / FA loading on decolorization rate

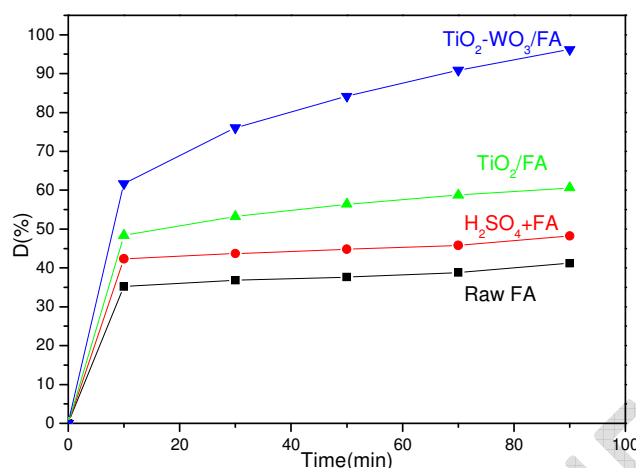


Fig.5 Effect of photocatalytic degradation time on decolorization rate

4. Conclusions

The surface of FA carrier was activated and modified by a simple wet-chemical method. The results showed that the activated FA increased specific surface area by H₂SO₄ soaking and the modified FA was more beneficial to loading photocatalysts via tetrabutyl titanate sol processing. The as-prepared TiO₂-WO₃/FA composite photocatalyst showed the higher photocatalytic degradation efficiency under UV irradiation. With the increasing of the TiO₂-WO₃ loading amount in the range wt0.5%-5%, the decolorization efficiency increases from 76% to 97% after 30 min. Further increasing the catalyst dosage from wt6%-10% resulting in a slight decrease in the decolorization efficiency. The wt0.5% (TiO₂-WO₃/FA) composite photocatalyst compared with raw FA, activated FA and modified FA. It indicated that the decolorization rate appeared gradually increasing with time extension and reached more than 97% at 90 min. The results revealed that the photocatalytic degradation plays a main role effectively after adsorption equilibrium.

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