

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 on methyl orange(MO) 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; methyl orange(MO)

Introduction

In recent years, the 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.

Fly ash(FA) as the solid by-product of coal-fired power plants, the main components are silica, alumina, ferrous oxide, and calcium oxide with varying amounts of carbon, the chemical composition is difference due to the type, source and combustion condition. The chemical composition containing a variety of oxides with SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, Na₂O, TiO₂ and so on. It was recognized to pose huge environmental problems (air, soil and water pollution,etc), therefore, more and more research are devoted to identifying various effective paths to use the fly 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, in soaking process, the soluble alkaline oxides (K₂O, Na₂O, MgO, CaO) and free inorganic component were removed from the raw FA into the solution, then, its surface was treated with butyl titanate sol, the modified FA was used as carrier for the immobilization of industrial nano-TiO₂-WO₃ photocatalyst. The composite photocatalytic (TiO₂-WO₃/FA) 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

42 considered .

43 **2. Experimental**

44 **2.1 Reagent and Instrument**

45 All chemicals were of reagent grade and were used without further purification. The FA was collected
46 from the electro-filters of the thermal power plant in Hebei Province Baoding City (ASTM C618-05,
47 China-2008). The $\text{TiO}_2\text{-WO}_3(\text{WO}_3, \text{wt } 3\%)$ powder were commercial product purchased from Jiangsu
48 Catalyst Co., Ltd.

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

55 **2.2 Activation and surface modification of FA**

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

62 **2.3 Preparation of nano- $\text{TiO}_2\text{-WO}_3$ /FA composites photocatalyst**

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

68 **2.4 Photocatalytic activity test**

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

77 **3. Results and discussion**

78 **3.1 XRD analysis**

79 The phase structure and crystal form of different as-prepared samples are performed by X-ray
80 diffraction. Fig.1 shows the XRD patterns of the raw FA, activated and modified FA and composite
81 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), the diffraction peak position and intensity have changed partly .Fig.1c shows the XRD pattern of composite photocatalyst. It can be seen that the new diffraction peaks at 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(TiO_2 - 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.

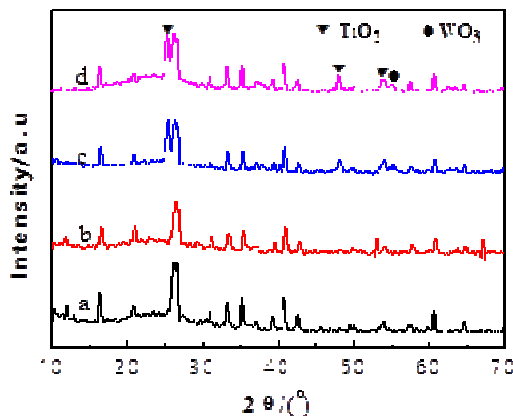


Fig.1 XRD spectra of samples(a:Raw FA; b: Activated and modified FA; c:composite photocatalyst ; d:After photocatalysis)

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 $15.5\text{m}^2/\text{g}$, which is larger than that of raw FA ($8.2\text{m}^2/\text{g}$). 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

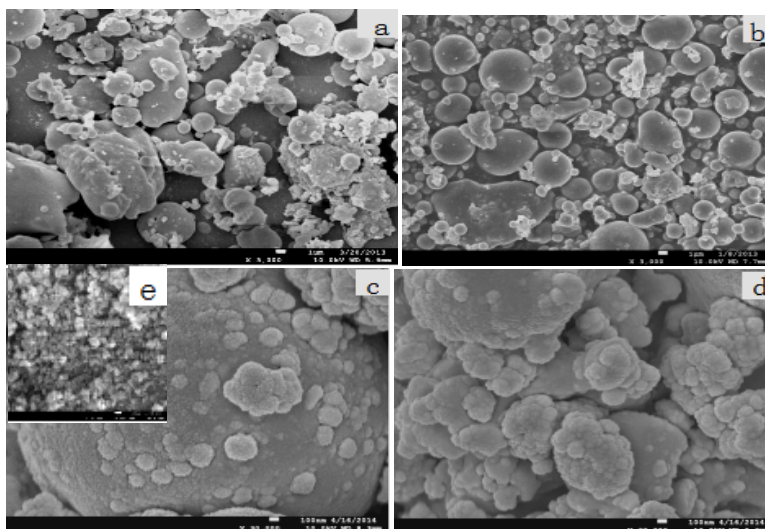


Fig.2 SEM photos (a: raw FA; b: activated FA; c:FA/ TiO_2 - WO_3 ; d:FA/ TiO_2 - WO_3 after photocatalysis; e: TiO_2 - WO_3)

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.2 b, 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(Fig. 2e). 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.

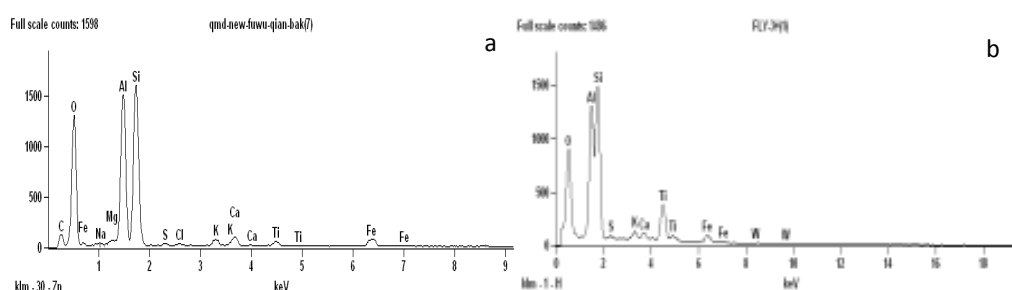


Fig.3 EDS spectrums of samples (a:raw FA; b: FA/TiO₂-WO₃/FA)

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), compared 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 modification 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 40w UV light irradiation [10]. The other condition was fixed with the 50 mL MO solution, 200 mg composite photocatalyst and 30min time. The photocatalytic activity were tested at the different TiO₂-WO₃ loading capacity. For investigating carrier effect of FA, firstly, the decolorization performance of activation and modify FA was tested under dark condition. The results show decolorization ratio is about 40%. This result confirmed that the FA carrier posses preferably adsorption performance. The Fig.4 show the photocatalytic activity of composite photocatalyst at the different TiO₂-WO₃ amount supported on FA. 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

156 efficiency is about 58%, when have not $\text{TiO}_2\text{-WO}_3$ composite photocatalyst. The reason was attributed to
157 excitation and modify FA by H_2SO_4 and titanium sol[11]. With the increasing of the $\text{TiO}_2\text{-WO}_3$ loading
158 amount in the range wt0.5%-5%, the decolorization efficiency increases from 76% to 97% after 90 min.
159 However, further increasing the catalyst dosage from wt6%-10% resulting in a slight decrease in the
160 decolorization efficiency. The reason may be a more photocatalyst suspension may lead to decrease of its
161 transparency resulting in less efficient radiation penetration [12]. In order to further investigate the
162 decolorization efficiency, the wt0.5% ($\text{TiO}_2\text{-WO}_3/\text{FA}$) composite photocatalysts was used to compare with
163 raw FA, activated FA and modified FA at different photocatalytic degradation time. The experimental
164 results were shown in Fig.5, under the same condition, the decolorization rate of activation FA exhibit
165 higher decolorization than raw FA in the first 10min. The decolorization rate was about 35% and 42%
166 respectively, with the increase of time, the decolorization rate was stable, it was inferred that the adsorption
167 process played a dominant role and reach adsorption-desorption equilibrium in 10 min. This results show
168 that the adsorptive property of activation FA possess have
169 good discoloring performance than raw FA due to the higher specific surface area. Compared with the
170 modify FA by tetrabutyl titanate sol, the degradation and discoloring rate can reach about 50% in 10min,
171 afterward, the discoloring rate emerge slowly increase with time increasing. The reason for the result was
172 that the anatase TiO_2 film supported on FA surface, the photocatalytic degradation play its role effectively
173 after adsorption equilibrium. In addition, it's worth noting that the highest degradation activity was shown
174 in Fig.5. A significant increase in photocatalytic activity is exhibited by the as-prepared composite
175 photocatalysts, the degradation and discoloring rate reach over 80% in 10min, the decolorization rate
176 appeared gradually increasing with time extension and reached more than 97% at 90min under UV
177 radiation. The results indicate that the as-prepared composite photocatalysts displayed excellent
178 photocatalytic performance. The reason may be attributed to the doping WO_3 presence in composite
179 photocatalysts. The TiO_2 and WO_3 simultaneously occur interband transitions under the UV irradiation
180 [13]. The photoinduced electron transfer from the TiO_2 surface to the lower energy level WO_3 due to
181 different energy levels, the WO_3 induced hole was migrated to the higher TiO_2 valence band, this process
182 suppressed the electron-hole pair recombination[14-16]. On the other hand, the photocatalytic process was
183 mainly carried out on the catalyst surface, a larger specific surface area FA carrier had been confirmed by
184 activating and modifying process, meanwhile some elements(Fe, S, etc) of FA carrier may be enhanced
185 photocatalytic activity due to improve the absorption threshold and reduce the hole-electron pair
186 recombination. In addition, the composite photocatalysts was carried out for 5 times, the degradation and
187 discoloring rate reached to 95% in 90min. So, the as-prepared composite photocatalysts showed the higher
188 photocatalytic degradation efficiency and stability.

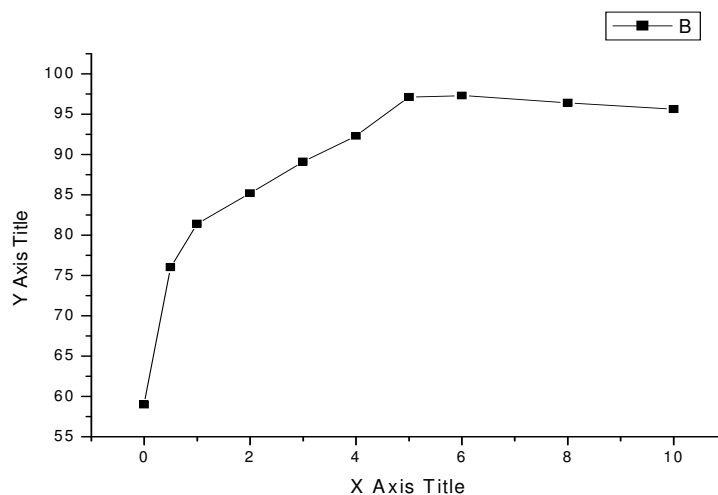


Fig.4 Effect of the different $\text{TiO}_2\text{-WO}_3$ supported amount on decolorization rate

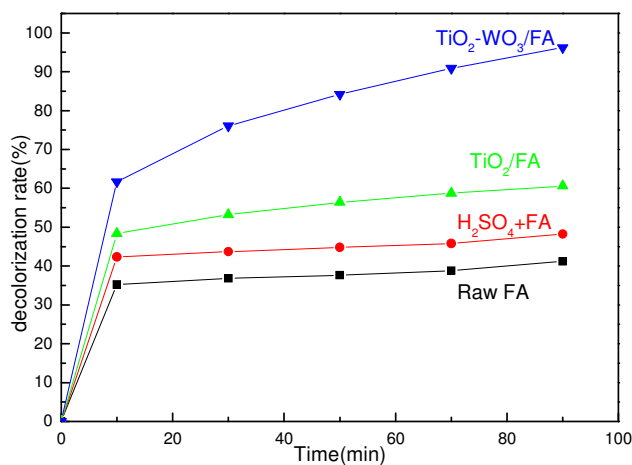


Fig.5 Effect of decolorization rate at photocatalytic degradation time

Conclusions

The surface of FA carrier was activated and modified by a simple wet-chemical method. The results showed that the specific surface area of activation FA was $15.5\text{m}^2/\text{g}$, which is larger than that of raw FA ($8.2\text{m}^2/\text{g}$) by H_2SO_4 soaking and the modified FA was more beneficial to loading photocatalysts via tetrabutyl titanate sol processing. The as-preparative $\text{TiO}_2\text{-WO}_3/\text{FA}$ composite photocatalysts showed the higher photocatalytic degradation efficiency under UV irradiation. With the increasing of the $\text{TiO}_2\text{-WO}_3$ 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% ($\text{TiO}_2\text{-WO}_3/\text{FA}$) composite photocatalysts 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 90min. The results revealed that the photocatalytic degradation play main role effectively after adsorption equilibrium. The result showed that the specific surface area of activation FA was $15.5\text{m}^2/\text{g}$, which is larger than that of raw FA ($8.2\text{m}^2/\text{g}$).

References

- [1] Yun Jeong Hwang, Sena Yang, Eun Hee Jeon, et al. Photocatalytic oxidation activities of TiO_2 nanorod arrays: A surface spectroscopic analysis[J]. *Applied Catalysis B: Environmental*, 2016, 180.
- [2] Kim Jihyun R, Kan Eunsung. Heterogeneous photocatalytic degradation of sulfamethoxazole in water using a biochar-supported TiO_2 photocatalyst[J]. *Journal of environmental management*, 2016, 180, 94-101.
- [3] Mohamad Mohsen Momeni, Yousef Ghayeb. Preparation of cobalt coated TiO_2 and $\text{WO}_3\text{-TiO}_2$ nanotube films via photo-assisted deposition with enhanced photocatalytic activity under visible light illumination[J]. *Ceramics International*, 2016.
- [4] Ferhat Dinçer, M. Hamdi Karaoğlu, Mehmet Ugurlu, et al. Ozonation of Reactive Orange 122 Using La^{3+} -Doped WO_3/TiO_2 /Sep Photocatalyst[J]. *Ozone: Science & Engineering*, 2016, 38(4), 291-301.
- [5] Quan Zhang, Fei Li, Xinyuan Chang, et al. Comparison of Nickel Foam/Ag-Supported ZnO , TiO_2 , and WO_3 for Toluene Photodegradation[J]. *Materials and Manufacturing Processes*, 2014, 29(7), 789-794.
- [6] Blissett R S, Rowson N A. A review of the multi-component utilisation of coal fly ash[J]. *Fuel*, 2012, 97(7), 1-23.
- [7] Wang M, Zhao H, Liu Y, et al. Removal of Fe from fly ash by carbon thermal reduction[J]. *Microporous & Mesoporous Materials*, 2017, 245, 133-137.
- [8] Martin L H J, Winnefeld F, Tschopp E, et al. Influence of fly ash on the hydration of calcium sulfoaluminate cement[J]. *Cement & Concrete Research*, 2017, 95, 152-163.
- [9] Khan M S, Prasad J, Abbas H. Effect of High Temperature on High-Volume Fly Ash Concrete[J]. *Arabian Journal for Science & Engineering*, 2013, 38(6), 1369-1378.
- [10] Taeseok Choi, Jung-Sik Kim, Jung Hyeon Kim. Influence of alkoxide structures on formation of TiO_2/WO_3 heterojunctions for photocatalytic decomposition of organic compounds[J]. *Advanced Powder Technology*, 2016.
- [11] P.N. Gaikwad, T.M. Wandre, K.M. Garadkar, et al. Improvement of photocatalytic activity of $\text{TiO}_2\text{-WO}_3$ nanocomposite by the anionically substituted N and S[J]. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016.
- [12] Y.M. Hunge, M.A. Mahadik, A.V. Moholkar, et al. Photoelectrocatalytic degradation of oxalic acid using WO_3 and stratified WO_3/TiO_2 photocatalysts under sunlight illumination[J]. *Ultrasonics - Sonochemistry*, 2016.
- [13] Francesca Riboni, Maria Vittoria Dozzi, Maria Cristina Paganini, et al. Photocatalytic activity of $\text{TiO}_2\text{-WO}_3$ mixed oxides in formic acid oxidation[J]. *Catalysis Today*, 2016.
- [14] P. V. S. Giri Babu, G. Swaminathan. Comparative Study on Synergetic Degradation of a Reactive Dye Using Different Types of Fly Ash in Combined Adsorption and Photocatalysis[J]. *Journal of The Institution of Engineers (India): Series A*, 2016, 97(3), 239-246.
- [15] Tengting Shi, Xiangyang Hao, Jiayi Ma, et al. Preparation of $\text{Ag}_2\text{O}/\text{TiO}_2$ /Fly-ash Cenospheres Composite Photocatalyst[J]. *Materials Letters*, 2016.
- [16] Lu Yang, Fazhou Wang, Dan Du, et al. Enhanced photocatalytic efficiency and long-term performance of TiO_2 in cementitious materials by activated zeolite fly ash bead carrier[J]. *Construction and Building Materials*, 2016.

