Fabrication of Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofibers by electrospinning and their enhanced photocatalytic activity

F Yang$^1$, X J Yu$^{1,2}$, T Zhang$^1$, J F Niu$^1$, J Li$^1$, J K Nie$^1$, J P Li$^1$ and B H Yao$^1$

$^1$School of Science, Xi’an University of Technology, Xi’an 710048, China

E-mail: yxjw@xaut.edu.cn

Abstract. Herein, Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofiber composites with different contents of Ag were prepared using electrospinning with a calcining process. The structure and morphology of Ag/TiO$_2$/Fe$_2$TiO$_5$ were characterized by TG-DTA, FT-IR, XRD, and SEM. The results shown that the organic template was completely decomposed at about 670°C. It can also find the rutile and anatase TiO$_2$ coexisted in TiO$_2$ nanofibers, but the peaks of anatase TiO$_2$ disappeared in Fe$_2$TiO$_5$/TiO$_2$. In addition, when Ag added in the Fe$_2$TiO$_5$/TiO$_2$, the peaks of Fe$_2$TiO$_5$ and TiO$_2$ have been strengthened greatly. It can conclude that the Fe$^{3+}$ and Ag$^+$ have an opposite effect on the crystal growing of the sample. In addition, the Ag nanoparticles (AgNPs) were well distributed in the surface of TiO$_2$/Fe$_2$TiO$_5$. The UV-Vis DRS and electrochemical tests indicated that the light absorption and carries separation of Ag/TiO$_2$/Fe$_2$TiO$_5$ were enhanced obviously. Since the surface plasmon resonance effect of AgNPs and synergistic effect, the as-prepared composite (the content of Ag was 3% mol) show a higher photocatalytic performance in degradation of Rhodamine B (RhB 99.6%) than that of pure-TiO$_2$ and TiO$_2$/Fe$_2$TiO$_5$.

1. Introduction

For the past few years, water pollution, one of the serious environment problems in the world, have got much attention [1,2]. Due to the widely use of dye and antibiotic in the industrial and life, there are more and more organic pollutants in the water body, which is a great threat to life [3-5]. It must be controlled and governed. The traditional methods not only have a very high requirement over the treatment conditions, but cannot clean the water entirely [6]. As a green technology, photocatalysis is an invaluable and cost reducing way, and have been widely used in the field of energy and environment [7,8].

When photocatalyst obtained energy, electrons are transited from valence band (VB) to conduction band (CB). The result of transition behaviour is the formation of carries (holes in VB and electrons in CB). Consequently, these carries will react with the H$_2$O and O$_2$ to yield reactive species such as superoxide anions (-O$_2^-$) and hydroxyl radicals (-OH), which can degrade the organic contaminants completely.

As a semiconductor photocatalyst, TiO$_2$ first discovered for hydrogen generation under UV-light irradiation in 1972 [9]. Since then, it was used in many fields. Nevertheless, the two main drawbacks: (1) have a broad band gap (3.2 eV) and only absorb the ultraviolet light (<400 nm) [10-12]; (2) the fast recombination of generated carries, limits its application in the visible photocatalytic filed [13-15]. Therefore, it is of great importance to construction the visible-light-driven semiconductor to enhance their photocatalytic activity. The band gap of Fe$_2$TiO$_5$ with a rhombohedral structure composed of Fe$_2$O$_3$ layer and TiO$_2$ layer is about 2.0 eV [16], and it is a promising candidate. However, the pure
semiconductor often has a vast photo-induced carries combination and a lower charge migration, which led to low photocatalytic performance. And some strategies should be designed to deal with it.

Recently, the noble metallic nanoparticles have attracted considerable attention to enhance the visible light activity of photocatalyst duo to their surface plasmon resonance effect [17-19]. Compared with the Au, Pt, and Pd, Ag is cheaper and easier to fabrication [20]. Consequently, some Ag-semiconductor systems, such as Ag-ZnO [21-23], Ag-TiO$_2$ [20,24,25], Ag-g-C$_3$N$_4$ [26,27], Ag-SrTiO$_3$ [28], and Ag-CdWO$_4$ [29], were constructed and used as the efficiency photocatalyst.

In this work, Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofiber composites were synthesized using the electrospinning with a calcining process. The compositions and morphology of as-prepared samples were studied. Finally, the photocatalytic activities of Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofibers composites were estimated by the RhB degradation under Xeon light irradiation.

2. Experimental

2.1. Preparation of TiO$_2$ and Ag/ TiO$_2$/Fe$_2$TiO$_5$

In a typical synthesis, 1.26 mmol of Fe(NO$_3$)$_3$·9H$_2$O (Ferric Nitrate) and C$_{18}$H$_{36}$O$_4$Ti (Tetrabutyl titanate) were dissolved in 1.27 g DMF with magnetic stirring at room temperature, and then 1.42 g CH$_3$COOH (Acetic Acid) and 2.60 g CH$_3$CH$_2$OH (Ethanol) were added into the mixture. Afterward, 0.37 g of PVP (polyvinyl pyrrolidone) and a certain amount of AgNO$_3$ (Silver Nitrate) (0% mol, 2.5 mol%, 5.0% mol, 7.5% mol, 10.0% mol, and 12.5% mol) were slowly added into the above solution. The as-prepared sols were eventually obtained after continuous stirring for 12 h. Finally, the precursor sols were transferred to a 10.0 ml syringe with a stainless steel needle set as anode, and the aluminum foil collector was set as the cathode when the electrospinning process was done. In the process of electrospinning, the tip-to-collector was 12 cm, the voltage was 18 kV and the flow rate of the spinning solution was 0.24 mL/h. After electrospinning, the obtained precursor nanofibers (labeled as FTA-X, X=0, 1, 2, 3, 4, 5) were calcined at 800°C with a heating rate of 1°C/min and maintained for 4 h in the furnace. The samples were cooled to room temperature naturally, and Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofibers (labeled as FTA-X) were obtained. Simply, TiO$_2$ nanofibers (labeled as TO-PVP for precursor nanofibers and TO for a calcined one) were prepared by adding C$_{18}$H$_{36}$O$_4$Ti in the precursor solution without other salts.

2.2. Characterization

The crystal structures of the products were analyzed using an XRD-6100 model X-ray diffractometer (XRD, Shimadzu, Japan). Fourier transform infrared spectra were obtained using an FTIR-8900 Fourier transform infrared spectrometer (FT-IR, Shimadzu, Japan). The morphology of the samples was characterized by a VEGA3SBH model scanning electron microscope (Tescan, Česko). Ultraviolet visible diffuse reflectance spectra were investigated using a TU-1901 model double beam ultraviolet-visible spectrophotometer (UV-Vis DRS, Beijing Purkinje General Instrument Co., Ltd., China).

Photocurrent measurements were performed on a CHI 660E model electrochemical workstation (Chenhua Instrument Co., Ltd., China). The calomel electrode, a Pt wire, and the samples spread on FTO served as the reference electrode, counter electrode and working electrode, respectively, in a three-electrode cell. For transient photocurrent response analysis, a xenon lamp and Na$_2$SO$_4$ (0.1 M) served as the light source and electrolyte, respectively.

2.3. Photocatalytic evaluation

The photocatalytic reactor consisted of a high-pressure xenon lamp (light source), quartz tube (container for the mixture), air-blowing tube (for mixing and increasing the dissolved oxygen content) and condenser pipe (for temperature control). In the photocatalytic process, 50 mg of catalyst was dispersed in 50 mL of 10 mg/L RhB and kept in the dark for 30 min to obtain absorption-desorption equilibrium between the photocatalyst surface and simulated pollutants. Next, the samples of the reaction solution were taken every 20 min and centrifuged. The absorbance of the supernatant solution
at the characteristic bands of 554 nm (RhB) was recorded. The degradation efficiency of RhB could be calculated by the following equation:

$$\eta = \frac{c_0 - c_t}{c_0} \times 100\%$$

where $c_0$ is the initial concentration of RhB and $c_t$ is the concentration of RhB at time $t$.

3. Results and discussion

3.1. Structure and morphology of samples

Figure 1(a) shows the thermal performance of the as prepared precursor nanofibers (FTA-3-PVP). The mass loss with the decalescence and discharge heat of the sample can be divided into three stages. Firstly, the volatilization of some residual solvents (DMF, Ethanol, HAc, H$_2$O) were taken place when the temperature was at 90°C, and it corresponding to a endothermic peak [30]. Secondly, most of the organic template (PVP) and residual material (NO$_3^-$, CH$_3$(CH$_2$)$_3$O-) were oxidized (possible reaction shows in equations (2) and (3)) before 670°C [31]. The total mass loss was about 80%. Thirdly, the structure of the sample changed from amorphous form to a crystal form since the mass loss have stopped (organic components were removed completely [32,33]) and the absorption of heat was continuing (phase change and solid phase reaction).

$$\text{PVP} + \Delta \text{O}_2 \rightarrow \text{CO}_2 + \text{NO}_2 + \text{H}_2\text{O}$$

(2)

$$\text{Fe(NO}_3)_3 + \text{AgNO}_3 + \text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti} \rightarrow \text{Fe}_2\text{TiO}_5 + \text{TiO}_2 + \text{Ag} + \text{CO}_2 + \text{NO}_2 + \text{H}_2\text{O}$$

(3)

Figure 1. (a) TG-DTA curve of FTA-3-PVP; (b) FT-IR spectra of FTA-3-PVP and FTA-3; (c) XRD patterns of TO, FTA-0, and FTA-3.

The FT-IR spectra of FTA-3-PVP and FTA-3 are exhibited in figure 1(b). Typically, the absorption band in the 3400-3500 cm$^{-1}$ is the O-H of H$_2$O [34,35]. As can be seen from curve, the nanofibers show a strong absorption peak at 1651 cm$^{-1}$ that attributable to the C=O stretching vibration modes of PVP. And the characteristic peaks at 1380 cm$^{-1}$, 1494 cm$^{-1}$, and 2937 cm$^{-1}$ are corresponding to the NO$_3^-$ ($\text{Fe(NO}_3)_3$), C-H [36] (PVP, C$_{16}$H$_{36}$O$_6$Ti). After calcining at 800°C, the peaks of precursor materials mentioned above disappeared thoroughly, and a new absorption band formed in the 400-800 cm$^{-1}$ which should be ascribed to the inorganic products.

To know the phase composition and the change of crystalline form, the XRD of samples were tested, showing in figure 1(c). The diffraction peaks of TO at 25.37 (101), 37.91(004), 48.16(200), 55.20(211), and 70.48(220) correspond to the anatase TiO$_2$ (A-TiO$_2$, JCPDS: NO. 73-1764) [37,38]. We can also find the typical peaks of rutile TiO$_2$ (R-TiO$_2$, JCPDS: NO. 76-0317) [39,40] at the 27.44 (110), 36.09 (102) and 54.34 (211) in TO. The patterns of FTA-0 and FTA-3 show that the Fe$_2$TiO$_5$ (JCPDS: NO. 73-1631) [41] and R-TiO$_2$ coexists in the nanofibers, but the peaks of A-TiO$_2$ disappeared in the samples. In addition, when Ag added in the Fe$_2$TiO$_5$/TiO$_2$, the peaks of Fe$_2$TiO$_5$ and
TiO$_2$ have been strengthened greatly. We can conclude that the Fe$^{3+}$ and Ag$^+$ have an opposite effect on the crystal growing of the sample.

The SEM images of TO-PVP (a), FTA-0-PVP(b), FTA-3-PVP(c), TO(d), FTA-0(e), and FTA-3(f) are displayed in figure 2, respectively. It can be found from figures 2(a)-2(c) that the diameter of precursor nanofibers (some nanobelts also exists in the sample) range from 300 nm to 500 nm and the sample have a smooth and uniform surface. After calcined (figures 2(d)-2(f)), because of the removing of PVP templates, the fibers don’t just slender (150-250 nm), but actually become shorten. What’s more, by contrasting the morphology of FTA-3 (figure 2(g)) and FTA-5(figure 2(g)), it can be clearly observed that Ag nanoparticles are anchored in the surface of FTA-5, but the same situation does not occur in the FTA-3. It can be ascribed the difference to the fact that the content of Ag in FTA-5 are so numerous that they cause the formation of big AgNPs in their surface. The EDX spectra of FTA-3 is displayed in figure 2(i). The O, Ti, Fe and Ag exist in the sample. Typically, the atomic ratio of Ti and Fe are 1:1, which consistent with the XRD.

Figure 2. (a)-(h) SEM images of as-prepared samples; (i) EDX spectra of FTA-3.

3.2. Optical and electrochemical properties

UV-Vis diffuse reflection was used to study the light absorption properties of as prepared samples, showing in figure 3(a). It is easy to see that the light with the wavelength less than 400 nm can be captured by TiO$_2$. After the Fe$_2$TiO$_5$ combined, the absorption ranges of TiO$_2$ have a huge expansion, which is attributed to the utilization of the visible light. In addition, the light absorption was slightly enhanced when Ag content was appropriate. Deeply, the band gap of samples have been got by the $(\alpha h\nu)^2$-hv plot which is achieved using the $(E_g-dh\nu)^{1/2}=h\nu$ [42], and the results show in figure 3(b), the $E_g$ of TO, FTA-0, FTA-3, and FTA-5 are about 3.32 eV, 2.44 eV, 2.33 eV, and 2.48 eV, respectively. Since the band gap of FTA-3 is the smallest, it will produce more $e^-/h^+$ pairs [43].

Figures 4(a) and 4(b) show the photocurrent and EIS testing curves of samples. The Ag/TiO$_2$/Fe$_2$TiO$_5$, on the one hand, exhibits a highest photocurrent, which may attribute to the effective charge separation caused by synergistic effect of TiO$_2$, Fe$_2$TiO$_5$, and Ag. On the other hand, the photocurrent generated by the ternary complex is more stable than other samples, suggesting the more efficiency of separation of the photogenerated carriers. Significantly, the addition of Ag increased
the conductivity of the as prepared photocatalyst (see from the EIS test). And the migration rate of photogenerated carries will be accelerated [44].

**Figure 3.** (a) UV-Vis DRS, (b) plots of $(\alpha h \nu)^{2}$ versus photon energy (h $\nu$), (c) photocurrent and (d) EIS tests of TO, FTA-0, FTA-3, and FTA-5.

**Figure 4.** (a) photodegradation rates of RhB over as-prepared samples under light irradiation; (b) UV-Vis absorbance spectra for RhB; (c) the effect of pH on the adsorption of FTA-3.

### 3.3. Photocatalytic activity

The photocatalytic performance of Ag/TiO$_2$/Fe$_2$TiO$_5$ and other samples was estimated by degradation of RhB under Xeon light irradiation. The results show in figure 4(a), as can be seen that the composites consisting of TiO$_2$ and Fe$_2$TiO$_5$ exhibit higher degradation rates than pure samples and the photocatalytic performance can further enhance when Ag added in the system. The improved photocatalytic performance can be put down to the enhancement of optical absorption and charge separation rate offered from the synergistic effect of Ag, TiO$_2$, and Fe$_2$TiO$_5$. As mentioned above, however, the overloading Ag result in the forming of too big AgNPs and reduce not only the availability of silver atoms but also the surface plasmon resonance effect. Therefore, with the increasing of Ag content, the degradation properties of ternary complexes first increase and then decrease. In addition, it can be seen from figure 4(b) that the UV-vis absorption peaks at 553 nm of RhB disappeared after photocatalytic reaction continuing for 100 mins. This may indicate that RhB is completely degraded (99.6%) by FTA-3 [45, 46]. Typically, pH has a great effect on adsorption property of photocatalysis in a photocatalytic process. The results are shown in figure 4(c). We can find that the adsorption property of the photocatalysis increases with the pH decreases. Nevertheless, adjusting pH is not conducive to practical application and the degradation property of the samples were evaluated in the neutral condition.

### 4. Conclusion

Ag/TiO$_2$/Fe$_2$TiO$_5$ nanofibers composites with different contents of Ag were prepared using electrospinning with a calcining process. The structure, morphology and the photocatalytic property of samples were characterized and evaluated. The results showed that the Fe$^{3+}$ and Ag$^{+}$ have an opposite effect on the crystal growing of the samples. And the Ag nanoparticles (AgNPs) were well distributed
in the surface of TiO$_2$/Fe$_2$TiO$_3$. Compared with the pure TiO$_2$ and Fe$_2$TiO$_3$, the optical absorption and e/h$^+$ separation of ternary composites are higher. In addition, since the surface plasmon resonance effect of AgNPs and synergistic effect, the as-prepared composites (the content of Ag was 3%mol) show a higher photocatalytic performance in degradation of RhB (99.6%) than that of other samples. Furthermore, the RhB was degraded completely by the FTA-3.

Acknowledgments
This work was supported by the National Science Foundation of China (No. 21576220), the Natural Science Foundation of Shaanxi Province (Nos. 2015JZ005, 2017JQ2033, and 2018JQ5202), and the Key Laboratory Research Project of Shaanxi Province (No. 17JS085).

References
[1] Ramezanalizadeh H, Peymanfar R and Khodamoradi-poor N 2019 Optik 180 113-24
[2] Chae S, Noeiaghaei T, Oh Y, Kim I S and Park J S 2019 Water Res. 149 421-31
[3] Wollenberger L, Halling-Sørensen B and Kusk K O 2000 Chemosphere 40 723-30
[4] Martinez J L 2009 Environ. Pollut. 157 2893-902
[5] Vanhulle S, Trovsaset M, Enaud E, Lucas M, Taghavi S, Van Der Lelie D, Aken B, Foret M, Onderwater R C A, Wesenberg D, Agathos S N, Schneider Y J and Corbisier A M 2008 Environ. Sci. Technol. 42 584-9
[6] Karimi A, Kazeminezhad I and Azizia S 2019 Ceram. Inter. 45 3441-8
[7] Masami N, Soichiro Y, Takahiro H, Wataru S, Hou H H, Yukihiro N, Yoshio N and Nobuo S 2017 Mater. Sci. Semicond. Process. 57 12-7
[8] Wang H L, Zhang L S, Chen Z G, Hu J Q, Li S J, Wang Z H, Liu J S and Wang X C 2014 Chem. Soc. Rev. 43 5234
[9] Fujishima A and Hond K 1972 Nature 238 7
[10] Zhao K, Lu Y, Lu N, Zhao Y H, Yuan X, Zhang H, Teng L H and Li F 2013 Appl. Surf. Sci. 285 616-24
[11] Yang J, Bai H Z, Tan X C and Lian J S 2006 Appl. Surf. Sci. 253 1988-94
[12] Zhang J W, Fu D F, Gao H Y and Deng L 2011 Appl. Surf. Sci. 258 1294-9
[13] Kochuveedu S T, Jang Y H and Kim D H 2013 Chem. Soc. Rev. 42 8467
[14] Zhou X M, Liu G, Yu J G and Fan W H 2012 J. Mater. Chem. 22 13137
[15] Chen Z Y, Fang L, Dong W, Zheng F G, Shen M R and Wang J L 2014 J. Mater. Chem. A 2 824
[16] Bassi P S, Chiam S Y, Gurudayal, Barber J and Wong L H ACS Appl. Mater. Interfaces 6 22490-5
[17] Ren S T, Zhao G L, Wang Y Y, Wang B Y and Wang Q 2015 Nanotechnology 26 125403
[18] Madkour M and Sagheer F A 2017 Opt. Mater. Express 7 158
[19] Mondal K and Sharma A 2016 RSC Adv. 6 83589
[20] Chang L H and Cho C P 2019 Mater. Chem. Phy. 223 683-93
[21] Vaiano V, Materangolo M, Murcia J J, Rojas H, Navío J A and Hidalgo M C 2018 Appl. Catal B: Environ. 225 197-206
[22] Ma X L, Li H, Liu T Y, Du S S, Qiang Q P, Wang Y H, Yin S and Sato T 2017 Appl. Catal. B: Environ. 201 348-58
[23] Kumar P S S, Manivel A and Anandan S 2009 Water Sci. Technol. 59 1423-30
[24] Singh J, Tripathi N and Mohapatra S 2019 Nano-Struct. Nano-Obj. 18 100266
[25] Plodinec M, Grečiš, I, Willinger M G, Hammad A, Huang X, Panžič I and Gajović A 2019 J. Alloys Compd. 776 883-96
[26] Chen M, Guo C S, Hou S, Wu L L, Lv J P, Hu C H, Zhang Y and Jian Xu 2019 J. Hazard. Mater. 366 219-28
[27] Ling Y, Liao G Z, Xu P and Li L S 2019 Sep. and Purif. Technol. 216 1-8
[28] Wu Y Q and He T 2018 Spectrochimica Acta A 199 283-9
[29] Yan Y, Xing H W, Han C C and Yang A 2017 Ceram. Inter. 43 3905-9
[30] Zhang Y F, Li J Y, Q Li, Zhu L, Liu X D, Zhong X H, Meng J and Cao X Q 2007 J. Colloid Interf. Sci. 307 567-71
[31] Lang L M and Xu Z 2013 ACS Appl. Mater. Interfaces 5 1698-703
[32] Yang G R, Yan W, Wang J N and Yang H H 2014 Mater. Lett. 122 117-20
[33] Yang G R, Wang L, Wang J N and Yan W 2017 Ceram. Inter. 43 71-6
[34] Ma D, Zhang Y X, Gao M C, Xin Y J, Wu J and Bao N 2015 Appl. Surf. Sci. 353 118-26
[35] Hosseini S R, Ghasemi S, Kamali-Rousta M and Nabavi S R 2017 Int. J. Hydrogen Energy 42 906-13
[36] Ghafari E, Feng Y N, Liu Y, Ferguson I and Lu N 2017 Compo. Part B Eng. 116 40-5
[37] Xu X Y, Wen S F, Mao Q N and Feng Y H 2019 J. Alloys. Compd. 773 927-33
[38] Wu Y C, Liu Z M, Li Y R, Chen J T, Zhu X X and Na P 2019 Mater. Lett. 240 47-50
[39] Zhao Y L, Song D M, Qiang Y H, Gu X Q, Zhu L and Song C B 2014 Appl. Surf. Sci. 309 85-9
[40] Soundarajan P, Sankarasubramanian K, Logu T, Sethuraman K and Ramamurthi K 2014 Mater. Lett. 116 91-4
[41] Gao X M, Li M W, Hou Y L and Wang C Y 2015 Mater. Res. Innov. 19 1-6
[42] Iqbal M, Ali A, Nahyoon N A, Majeed A, Pothu R, Phulpoto S and Thebo K H 2019 Mater. Sci. Energy Technol. 2 41-5
[43] Shu Z, Zhang Y, Ouyang J and Yang H M 2017 Appl. Surf. Sci. 420 833-8
[44] Qin N, Xiong J H, Liang R W, Liu Y H, Zhang S Y, Li Y H, Li Z H and Wu L 2017 Appl. Catal. B: Environ. 202 374-80
[45] Cao Q W, Zheng Y F and Song X C 2017 J. Taiwan Inst. Chem. E. 70 359-65
[46] Liu G, Wang G H, Hu Z H, Su Y R and Li Zhao 2019 Appl. Surf. Sci. 465 902-10