

# Visible light photocatalytic degradation of Methyl orange by $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ coated self-cleaning cotton

F. ZHENG<sup>a</sup>, D. WU<sup>a,b\*</sup>, J. XIA<sup>a</sup>, Y. TAN<sup>a</sup>

<sup>a</sup>Science and Technology College of Hubei University for Nationalities, Enshi, Hubei Province, 445000, China

<sup>b</sup>School of Chemical and Environmental Engineering, Hubei University for Nationalities, Enshi, Hubei Province, 445000, China

The visible-light-induced photocatalytic performance of  $\text{TiO}_2$ -cotton has been realized by loading  $\text{Ag}_3\text{PO}_4$  particles. The physical properties were characterized by means of SEM, XPS and DRS techniques. The photocatalytic activities of the samples were evaluated for the degradation of methyl orange under visible light irradiation. In comparison with  $\text{TiO}_2$ -cotton, the dramatic enhancement in the photocatalytic performance of the  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton could be attributed to the synergistic effect of  $\text{BiOI}$  and  $\text{TiO}_2$ .  $\text{Ag}_3\text{PO}_4$  can generate electron-hole pairs under visible light irradiation and  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$  heterojunction can reduce the recombination of photogenerated charge carriers, resulting in high quantum efficiency and excellent photocatalytic properties.

(Received July 4, 2015; accepted September 9, 2015)

**Keywords:**  $\text{Ag}_3\text{PO}_4$ ,  $\text{TiO}_2$ , Heterojunction, Visible light, Photocatalysis

## 1. Introduction

During the past several years, immobilization of photocatalyst nanoparticles onto textile materials has been interested to produce goods with multifunctional properties such as UV protective, self cleaning and antibacterial [1 2]. Coating the surface with photocatalyst nanomaterials could enable it to possess the ability of decomposing organic substance, killing pathogenic microorganisms and removing stains by utilizing the free and abundant sunlight [3, 4], because photocatalyst can absorb energy equal to or more than its energy gap to generate electron-hole pairs and then form superoxide anion and hydroxyl radical, which can trigger a series of reductive and oxidative reactions.  $\text{TiO}_2$  is the most frequently studied and popular photocatalyst due to its merits of nontoxicity, high photoactivity, photo- and chemical stability, and low production cost. So far,  $\text{TiO}_2$  NPs have been immobilized successfully on different sorts of textile fibers to enable them to possess self-cleaning ability [5, 6]. Among the various immobilized techniques, the sol-gel coating method is a convenient way to form  $\text{TiO}_2$  coatings over various substrates with low thermal resistance. Recently, we have successfully prepared  $\text{TiO}_2$ -coated cotton fabrics at low temperature, which possesses excellent self-cleaning properties for sterilization of bacteria and decoloration of methyl orange [7].

However, the intrinsic wide band gap of  $\text{TiO}_2$  and the relatively high rate of electron-hole recombination often result in a low quantum yield and poor efficiency of photocatalytic reactions. Therefore, there is a need to develop an effective means of improving the visible-light photoactivity and charge separation efficiency. Forming a heterojunction by combination of  $\text{TiO}_2$  with a narrow band gap semiconductor was demonstrated to be an effective way to fabricate  $\text{TiO}_2$ -based catalysts with extended absorption of visible light and higher photocatalytic activity [8]. Recently, semiconductor  $\text{Ag}_3\text{PO}_4$  with a band gap of ca.2.45 eV has attracted considerable attention due to its high photocatalytic efficiency in the visible light region [9, 10]. Moreover, its conduction band (CB) and valence band (VB) edge potentials are 0.45 eV and 2.9 eV (vs.NHE), respectively [11, 12], and its CB potential is lower than that of  $\text{TiO}_2$  with -0.26 eV. Therefore  $\text{Ag}_3\text{PO}_4$  is considered to be an appropriate sensitizer to improve photocatalytic activity in the  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$  system.

Therefore, to enhance the photocatalytic self-cleaning property of  $\text{TiO}_2$ -cotton prepared by a dip-pad-dry-cure process,  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton has been successfully fabricated by loading  $\text{Ag}_3\text{PO}_4$  photocatalysts on the surface of  $\text{TiO}_2$ -cotton. The prepared samples showed high visible-light photocatalytic activity and the photocatalytic mechanism has been discussed in detail.

## 2. Experimental

### 2.1. Materials

Tetrabutyl titanate (Ti(OBu)<sub>4</sub>), silver nitrate (AgNO<sub>3</sub>), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O), dipotassium phosphate (K<sub>2</sub>HPO<sub>4</sub>), nitric acid (HNO<sub>3</sub>) and ethanol (C<sub>2</sub>H<sub>5</sub>O) were purchased from Sinopharm Chemical Reagent Co. Ltd. All chemicals were analytical grade without further purification. Deionized water was used throughout this study.

### 2.2. Preparation of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>-cotton

Coating of TiO<sub>2</sub> films on cotton (TiO<sub>2</sub>-cotton) was prepared by the method described in our earlier study [7]. Loading Ag<sub>3</sub>PO<sub>4</sub> on the TiO<sub>2</sub>-cotton was carried out by a once sequential chemical bath deposition in [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> and K<sub>2</sub>HPO<sub>4</sub> aqueous solution. Firstly, TiO<sub>2</sub>-cotton was immersed in a 0.01 M [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> solution for 1 h in order to adsorb large numbers of Ag<sup>+</sup> ions as much as possible on the surface. Then, the treated cotton was dipped into a 0.01M K<sub>2</sub>HPO<sub>4</sub> solution for 1 h so that the absorbed Ag<sup>+</sup> ions on the cotton fabrics react with PO<sub>4</sub><sup>3-</sup> to generate Ag<sub>3</sub>PO<sub>4</sub> particles. Lastly, the cotton fabrics were washed by a mass of water to remove unattached Ag<sub>3</sub>PO<sub>4</sub> particles from the fabric surface, and then can be used to test the properties after natural drying.

### 2.3. Characterization of catalysts

X-ray powder diffraction (XRD) pattern of samples were recorded on a powder X-ray diffractometer (D/max-2200/PC, Rigaku Corporation, Japan) with Cu K<sub>α</sub> radiation, operating at 40 kV and 30 mA, where λ=0.15418 nm for the Cu K<sub>α</sub> line. XPS experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer, USA), the shift of the binding energy due to relative surface charging was corrected using the C 1s level at 284.6 eV as an internal standard. The structure and morphology of the coatings were investigated by the field emission scanning electron microscopy (FESEM, FEI SIRION 200, FEI, USA). UV-Vis diffuse reflectance spectra (DRS) of the samples were recorded on a UV-Vis spectrophotometer (TU-1901) with an integrating sphere attachment. The analyzed range was 230-800 nm, and BaSO<sub>4</sub> was used as a reflectance standard.

### 2.4. Photocatalytic degradation of MO

Methyl orange (MO) was selected as a model chemical to evaluate the activity of the catalysts. A 300 W Xe lamp was used as the light source of a homemade photoreactor, surrounded with a water circulation facility at the outer wall through a quartz jacket. The short wavelength components (λ < 420 nm) of the light was cut off using a glass optical filter. Before irradiation, 60 ml MO solution (10 mg/L) with a piece of 4 cm × 4 cm Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>-cotton was stirred in the dark for 30 min to achieve adsorption equilibrium. MO solution was taken out at regular time intervals and the residual MO concentration was monitored at 464 nm using a UV-vis spectrophotometer (UNICO 7200).

## 3. Results and discussion

Fig.1 shows the SEM images of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>-cotton, TiO<sub>2</sub> thin layer attached to the cotton substrate has been formed, and Ag<sub>3</sub>PO<sub>4</sub> nanoparticles were successfully loaded on the TiO<sub>2</sub> surface. The XPS was carried out to investigate the surface compositions and chemical state of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>-cotton. The Ag3d spectra of Ag<sub>3</sub>PO<sub>4</sub> was composed of two individual peaks at ~374 and ~368 eV (Fig.2a), which could be attributed to Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> binding energies, respectively [9, 13]. Moreover, the binding energy of P2p is 133.54 eV(Fig.2b), which is consistent with that (133.50 eV) coming from the PO<sub>4</sub><sup>3-</sup> [13].

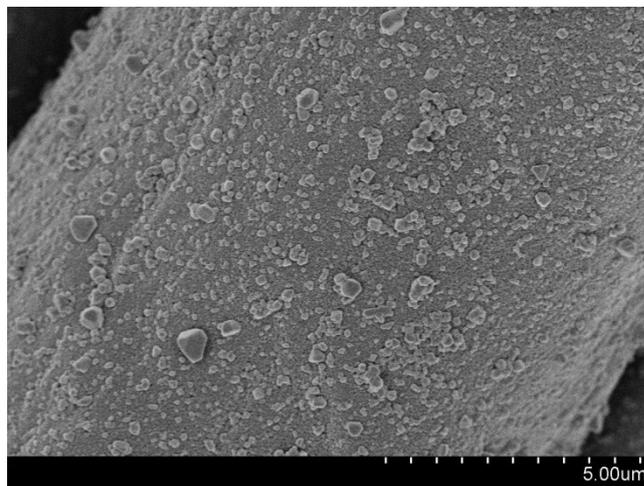


Fig.1 SEM images of Ag<sub>3</sub>PO<sub>4</sub>/TiO<sub>2</sub>-cotton.

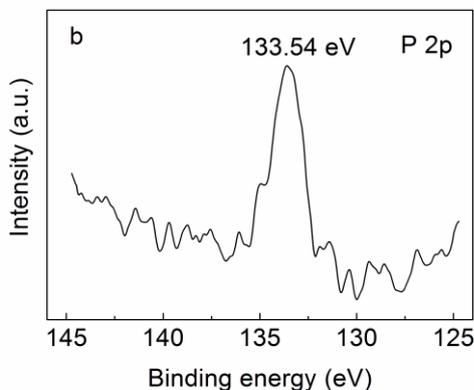
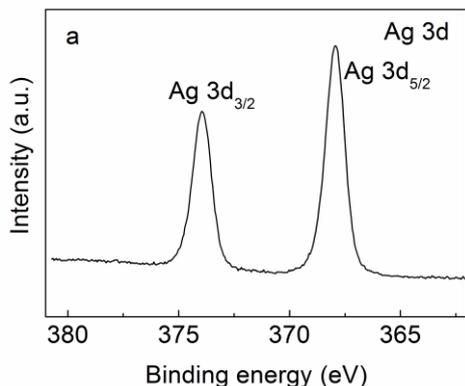


Fig.2 XPS spectra of the  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton: (a) Ag 3d and (b) P 2p.

UV-Vis diffuse reflectance spectra of the as-prepared samples are shown in Fig.3. The  $\text{TiO}_2$ -cotton only has absorbance in the UV light range with an absorption edge about 382 nm. Whereas the  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton shows strong absorption in the visible light range, with the absorption edge round 505 nm, which is attributed to the  $\text{Ag}_3\text{PO}_4$  on the surface of  $\text{TiO}_2$  films. Meanwhile, the band gap of  $\text{Ag}_3\text{PO}_4$  can be calculated by the following equation [14]:

$$\alpha h\nu = A (h\nu - E_g)^{n/2} \quad (1)$$

Where  $\alpha$ ,  $\nu$ ,  $E_g$  and  $A$  are absorption coefficient, light frequency, band gap, and a constant, respectively. Among them,  $n$  is determined by the type of optical transition of a semiconductor (i.e.,  $n=1$  for direct transition and  $n=4$  for indirect transition). The  $n$  value for  $\text{Ag}_3\text{PO}_4$  is 4, because  $\text{Ag}_3\text{PO}_4$  is indirect semiconductor<sup>10</sup>. Therefore, the estimated band gap energy of  $\text{Ag}_3\text{PO}_4$  was about 2.43 eV (Fig.5).

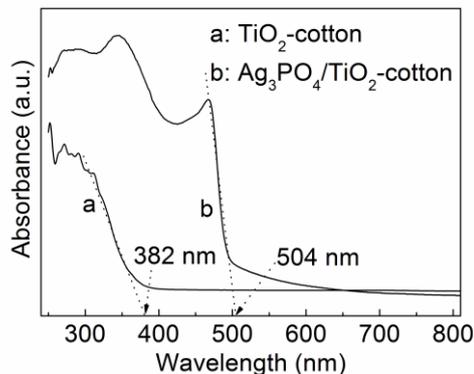


Fig.3 UV-vis diffuse reflectance spectra of (a)  $\text{TiO}_2$ -cotton and (b)  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton.

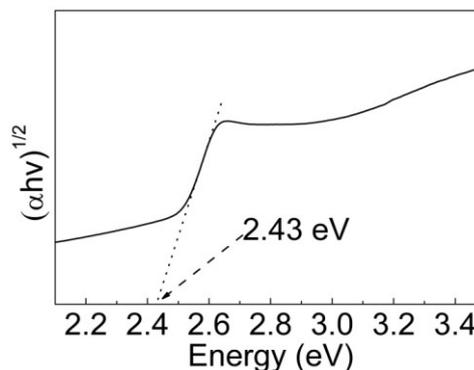


Fig.4. Plots of  $(\alpha h\nu)^{1/2}$  vs photon energy ( $h\nu$ ) for the band gap energy of  $\text{Ag}_3\text{PO}_4$ .

The photocatalytic activity of  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton was measured by decomposing methyl orange (MO) under visible irradiation. Fig.6 shows the photodegradation of MO dye as a function of irradiation time over different samples. Under visible light irradiation for two hours, the photodegradation of MO over  $\text{TiO}_2$ -cotton is very weak, and the MO removal over  $\text{Ag}_3\text{PO}_4$ -cotton and  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton reached 26% and 37%, respectively. It is well-known that photocatalytic oxidation of organic pollutants follows first-order kinetics. The reaction rate constant can be fitted by the following equation

$$\ln(C_0/C) = k t \quad (2)$$

Where  $C$  is the concentration of the MO aqueous solution at reaction time  $t$ ,  $C_0$  is the initial MO concentration, and  $k$  is the reaction rate constant. A good linear relationship was observed between  $\ln(C_0/C)$  and irradiation time (Fig.6). The MO degradation rate constants were calculated as  $0.00016 \text{ min}^{-1}$ ,  $0.0025 \text{ min}^{-1}$  and  $0.0038 \text{ min}^{-1}$  for  $\text{TiO}_2$ -cotton,  $\text{Ag}_3\text{PO}_4$ -cotton and  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton,

respectively. The  $k$  value of  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton was estimated to be about 1.52 times higher than that of  $\text{Ag}_3\text{PO}_4$ -cotton. The outstanding visible-light-induced photocatalytic activity of  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton should be attributed to the synergistic effect of  $\text{TiO}_2$  and  $\text{Ag}_3\text{PO}_4$ . Due to its narrow band gap energy,  $\text{Ag}_3\text{PO}_4$  can be efficiently excited by visible light to generate electron-hole pairs and form reactive oxygen species of  $\cdot\text{OH}$  and  $\text{O}_2\cdot^-$  radical, which have strong oxidizing ability to decompose almost all organic pollutants [15, 16]. Meanwhile, a heterojunction can be formed at the interface of  $\text{TiO}_2$  and  $\text{Ag}_3\text{PO}_4$ , which is good for reducing the recombination of photogenerated charge carriers [17, 18], resulting in high quantum efficiency and excellent photocatalytic properties.

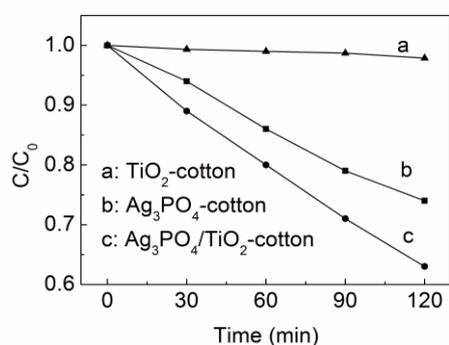


Fig.5 Photocatalytic activities of  $\text{TiO}_2$ -cotton (a),  $\text{Ag}_3\text{PO}_4$ -cotton (b) and  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton (c).

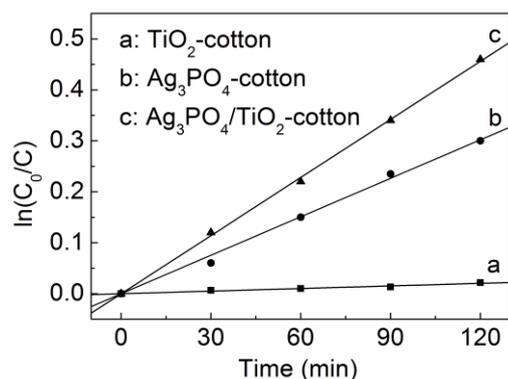


Fig.6 Pseudo-first-order kinetics of  $\text{TiO}_2$ -cotton (a),  $\text{Ag}_3\text{PO}_4$ -cotton (b) and  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton (c).

#### 4. Conclusions

$\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton has been successfully fabricated by coating  $\text{TiO}_2$  films and loading  $\text{Ag}_3\text{PO}_4$  particles through a facile and effective method at low temperature. Because of narrow band gap,  $\text{Ag}_3\text{PO}_4$  can generate electron-hole pairs under visible light irradiation, and

$\text{Ag}_3\text{PO}_4/\text{TiO}_2$  heterojunction facilitates the transfer of the photoinduced carriers and reduce the recombination of electron-hole pairs. The prepared  $\text{Ag}_3\text{PO}_4/\text{TiO}_2$ -cotton displays outstanding photocatalytic activity under visible light irradiation.

#### Acknowledgments

This project was funded by Foundation of Hubei Provincial Department of Education (B2015106) and Undergraduate Innovation Program in Science and Technology College of Hubei University for Nationalities (k201439, 201413250003).

#### References

- [1] G. Sun., K. H. Hong, *Text. Res. J.* **83**(5), 532 (2013).
- [2] B. Tan, B. Gao, J. Guo, et al., *Surf. Coat. Technol.* **232**, 26 (2013).
- [3] S. Ortelli, M. Blosi, S. Albonetti, et al., *J. Photochem. Photobiol., A*, **276**, 58 (2014)
- [4] S. Afzal, W. A. Daoud, S. J. Langford, *ACS Appl. Mat. Interfaces*, **5**(11), 4753 (2013)
- [5] A. Sobczyk-Guzenda, H. Szymanowski, W. Jakubowski, et al., *Surf. Coat. Technol.* **217**, 51 (2013).
- [6] R. Rahal, T. Pigot, D. Foix, et al., *Appl. Catal. B: Environ.*, **104** (3), 361 (2011).
- [7] D. Y. Wu, M. C. Long, J. Y. Zhou, et al., *Surf. Coat. Technol.*, **203**(24), 3728 (2009).
- [8] J. Liu, L. Ruan, S. B. Adeloju, et al., *Dalton Trans.*, **43**(4), 1706 (2014).
- [9] Ma, J., Zou, J., Li, L., et al., *Appl. Catal. B: Environ.*, **144**, 36 (2014).
- [10] F. J. Zhang, F. Z. Xie, S. F. Zhu, et al., *Chem. Eng. J.*, **228**, 435 (2013).
- [11] Z. Yi, J. Ye, N. Kikugawa, et al., *Nat. Mater.* **9**, 559 (2009).
- [12] C. Dong, K.-L. Wu, M.-R. Li, et al., *Catal. Commun.*, **46**, 32 (2014).
- [13] D. Wang, Z. Li, L. Shang, et al., *Thin Solid Films*, **551**, 8 (2014).
- [14] M. A. Butler, D. S. Ginley, *J. Electrochem. Soc.*, **125**(2), 228 (1978)
- [15] X. Guan, J. Shi, L. Guo, *Int. J. Hydrogen Energy*, **38**(27), 11870 (2013).
- [16] W. Wang, B. Cheng, J. Yu, et al., *Chemistry-an Asian Journal*, **7**(8), 1902 (2012).
- [17] G. Fu, G. Xu, S. Chen, et al., *Catal. Commun.* **40**, 120 (2013).
- [18] Z. Chen, W. Wang, Z. Zhang, et al., *The Journal of Physical Chemistry C* **117**(38), 19346 (2013).

\*Corresponding author: wdy001815@126.com