IMMOBILIZATION OF POLYMER DOTS GRAFTED TiO_2 NANOHYBRIDS ON GAUZE FOR PHOTO DEGRADATION OF ORGANIC POLLUTANTS

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ABSTRACT

TiO_2, one of the most promising photocatalysts, is widely used in air purification, sewage treatment, water splitting, carbon dioxide reduction, and solar cells. However, TiO_2 can only absorb ultraviolet light, which makes up only a small fraction (< 4%) of the total solar spectrum, and TiO_2 nanoparticles are difficult to separate from water. These two problems seriously restrict the application of TiO_2 nanoparticles. Therefore, we successfully prepared polymer dots grafted TiO_2 nanohybrids (PDs-TiO_2) which possess excellent photocatalytic activity under visible light irradiation. We also successfully immobilized PDs-TiO_2 on the surface of Gauze by using thermal crosslinked PVA as the binder. TGA shows that the amount of TiO_2 immobilized on the surface of Gauze is about 1.8%. FTIR shows that the immobilized process and heat treatment process have no effect on gauze. Under visible light irradiation, the degradation rate of methyl orange on Gauze-PDs-TiO_2 was about 5.0 times higher than that on Gauze-TiO_2. This novel design of Gauze-PDs-TiO_2 is simple, green and effective, and may open up a new avenue for fabricating high performance visible light photocatalysts and facilitating their practical application.

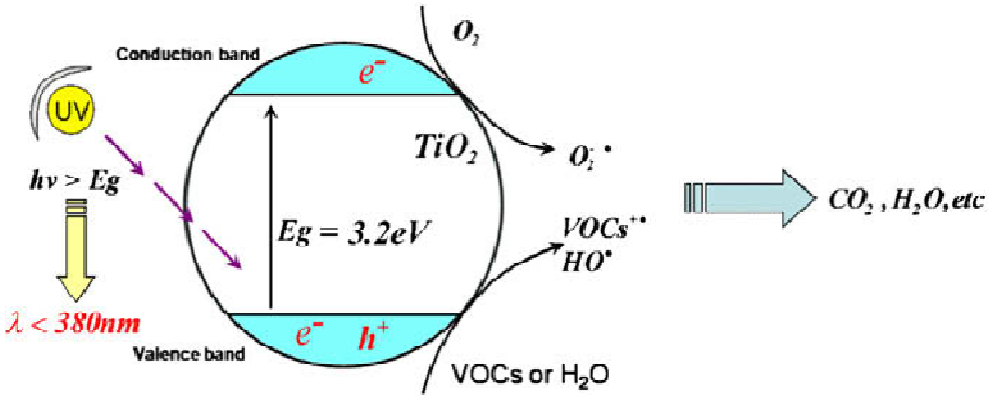
KEYWORDS

TiO_2, polymer dots, Gauze, photocatalyst, immobilization

1. INTRODUCTION

Titanium dioxide (TiO_2) is considered to be one of the best performing white pigments in the world and is widely used in coating, plastic, paper-making, synthetic fiber, cosmetic, and other fields. Unlike materials such as silicon dioxide, calcium carbonate,or clay, TiO_2 has a unique photocatalytic function, and its photocatalysis principle is shown in Scheme 1 [1]. Whether in water or in air, when TiO_2 is exposed to sunlight, especially ultraviolet light, the electrons on the valence band will be excited to transfer to the conduction band, resulting in free electron hole pairs which have strong redox ability and are capable of activating oxygen and water in the air to produce reactive oxygen and hydroxyl radicals. When pollutants such as benzene, methylbenzene, formaldehyde, bacteria and viruses are adsorbed on the surface of TiO_2, they are

combined with the reactive oxygen and hydroxyl radicals and decomposed into carbon dioxide and water through oxidation-reduction reaction. Therefore, TiO_2 is one of the most promising photocatalysts at present, and is widely used in air purification, sewage treatment, water splitting, carbon dioxide reduction, solar cells, and other fields [2].



Scheme 1 Photocatalytic mechanism of TiO_2 under ultraviolet Light[1]

As the particle size of TiO_2 decreases, the specific surface area and photocatalytic activity of TiO_2 increases. Therefore, nano-TiO_2 particles are more suitable for photo degradation of organic pollutants than micron TiO_2 particles. However, TiO_2 nanoparticles are difficult to separate from water. If it cannot be recycled, the TiO_2 nanoparticles will disperse into the natural environment, posing a potential threat to ecosystem and human health. In order to overcome the above application bottleneck, many efforts have been devoted to immobilizing TiO_2 nanoparticles on a variety of substrates[3], such as glass, stainless steel plate, clay, aluminum foil, carbon fiber film, polyethylene terephthalate and polypropylene [4]. Shang et al. [5] coated TiO_2 sol on the surface of stainless steel wire mesh, after calcination treatment, the immobilized TiO_2 with high specific surface area and high catalytic activity was obtained, and the results shown that this kind of immobilized TiO_2 has a good photocatalytic effect on formaldehyde. Zhang et al. [6] coated the PVA/TiO_2 composite photocatalyst on the honeycomb ceramic and attempted to prepare a kind of immobilized photocatalyst with high activity.

In recent years, many studies have been carried out on self-cleaning fabrics materials. For example, Shiva et al. [7] treated polyester fabric with alkali liquor and surfactant to form some pores and hydrophilic groups on the surface of polyester fiber, and then immersed the fabric in a dispersion liquid of TiO_2 nanoparticles. After ultrasonic and high temperature treatment, the fabric had a good catalytic effect on methylene blue. Qi et al. [8] prepared anatase TiO_2 sol with sol-gel method, and then put the plasma-treated polyester fabric into the TiO_2 sol. After heat treatment, the fabric which supports TiO_2 was obtained. Under fluorescent lamp, the fabric not only is capable of degrading colorant, red wine and coffee stains, but also has the bactericidal property.

Polyvinyl alcohol (PVA) is a kind of water-soluble polymer material containing a large amount of hydroxyl groups, and has been widely used in fiber, film, emulsifier, binder and other fields for its excellent film forming property, water solubility, mechanical property and biodegradability. PVA is commonly used as sizing agent for fiber spinning, which can be well coated on the surfaces of fibers. Pure PVA film is transparent in ultraviolet and visible light, so PVA is suitable

for supporting TiO_2 nanoparticles [9]. In our previous articles, Li et al. [10] successfully prepared polymer dots grafted TiO_2 nanohybrids (PDs-TiO_2) with high visible-light photocatalytic activity. As far as we know, there are no reports concerning using PVA as a binder to immobilize the modified TiO_2 on the surface of the Gauze.

Herein, we prepared PDs-TiO_2 firstly and mixed PDs-TiO_2 with PVA solution, and then immersed the Gauze in the mixed solution to adsorb a certain amount of the mixed solution. After heat treatment, the PVA was crosslinked and the Gauze which supports PDs-TiO_2 (Gauze-PDs-TiO_2) was obtained. The shape, structure and photocatalytic property of Gauze-PDs-TiO_2 were then investigated.

2. EXPERIMENTAL

2.1. Materials

PVA (average polymerization degree of 1750±50) was purchased from Beijing Yili Fine Chemical Co., Ltd, China. Titanium sulfate ($Ti(SO_4)_2$, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd, China. Sulfuric acid (AR) was obtained from Beijing Chemical Reagent Co., Ltd, China. Methyl orange (MO), used as the model pollutant, was manufactured by Zhejiang Yongjia Fine Chemical Plant, China. Gauze was obtained from Hua Lu Eisai Co., Ltd, China. All chemicals were used without further purification.

2.2. Synthesis of polymer dots (PDs)

4 g PVA was mixed with 396 mL deionized water in a 500 mL round flask under continuously stirring for 3 h at 95 ℃. The obtained PVA solution was colorless and transparent. Then 70 g of PVA solution was transferred to a 100 mL Teflon autoclave and heated up to 220 ℃ with a rate of 3 ℃/min. After reacting at 220 ℃ for 6 h, the reactor was cooled down to room temperature naturally. The obtained PDs solution was yellow and transparent.

2.3. Preparation of PDs-TiO2 nanohybrids

10 g PDs solution and 2 g $Ti(SO_4)_2$ were mixed with 56 g deionized water in a 100 mL Teflon autoclave, and 2 g Sulfuric acid was added dropwise into the autoclave under continuously stirring. The mixture was kept stirring for 30 min at room temperature to obtaina transparent homogenous solution. Then the autoclave was heated up to 200 ℃ with a rate of 3 ℃/min. After reacting at 200 ℃ for 6 h, the autoclave was cooled down to room temperature naturally. The resulting PDs-TiO2 nanohybrids were collected by centrifugation and then washed with deionized water for four times. Finally, the nanohybrids were dried under vacuum at 100 ℃ overnight. Pure TiO2 was synthesized by the same process in the absence of PDs solution.

2.4. Preparation of Gauze-PDs-TiO2

300 mg TiO_2 and 20mL deionized water were put into a 150 mL beaker, and the mixture was stirred for 2 min under ultrasonic dispersion. Then 40g PVA aqueous solution (7.5 wt%) was add into the system, and PVA/TiO_2 solution was obtained after stirring for another 15min. A piece of Gauze (20 cm× 20 cm, about 3.5g) was immersed into the above solution. After adsorption for about 5 min, the Gauze was taken out and the excessive solution was screw off by hands. The

amount of solution adsorbed by each piece of Gauze was about 10g. Then the Gauze was put on a glass plate and let it dry naturally. Finally, the Gauze-TiO_2 was obtained after the Gauze crosslinked under vacuum at 140 ºC for 2h. Gauze-PDs-TiO_2 was prepared in the same manner.

2.5. Characterization

Morphology of PDs-TiO_2 and Gauze-PDs-TiO_2nanohybrids was characterized by a transmission electron microscopy (TEM, HT7700,Hitachi) and a field emission scanning electron microscope (SEM, SU8020, Hitachi).

Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet 6700 spectrophotometer equipped with an attenuated total reflectance device (Smart Orbit), the resolution of the spectra was 4 cm^{-1}, and scans were repeated 32 times.

The contents of TiO2 in Gauze-PDs-TiO_2 was characterized by thermal gravimetric analysis (TGA, PerkinElmer) under air atmosphere with air flow of 20 mL/min, about 3mg sample was heated up to 700^{o}C at a heating rate of 20 ^{o}C/min.

2.6. Photocatalytic degradation

The photocatalytic activity of the samples was evaluated from the degradation rate of MO in aqueous solution with an initial concentration of 15 mg/L. In a typical photodegradation experiment, 40 mLMO solution and the sample photocatalyst containing 25 mg TiO_2 was placed in a 50 mL beaker. Prior to irradiation, the suspension was put in dark for 2 hours to establish adsorption-desorption equilibrium between dye and photocatalyst. The light source was a 500 W Xenon lamp equipped with an ultraviolet cut off filter (λ> 420 nm). At regular times, 5 mL suspension was put out and examined by measuring the absorption at 465 nm using an UV-Vis spectrophotometer (Lovibond, ET99731). MO degradation efficiency was calculated by the ratio of concentration (C_t/C_0, C_t and C_0 can be calculated by the absorbance intensity).

3. RESULTS AND DISCUSSION

The morphology and particle size distribution of pure TiO_2 and PDs-TiO_2 were studied by TEM. TEM image of TiO2is shown in Figure 1(A), demonstrating that the prepared TiO_2 are irregular shape particles with a diameter of about 20 nm, and the surface of pure TiO_2 particlesissmooth. The TEM image of PDs-TiO_2 is shown in Figure 1(B), revealing that many black dots are attachedto the surface of TiO_2, and the average size of these black dots is about 5 nm, which is consistent with that of PDs. This indicates that the PDs-TiO_2 particles were successfully prepared.

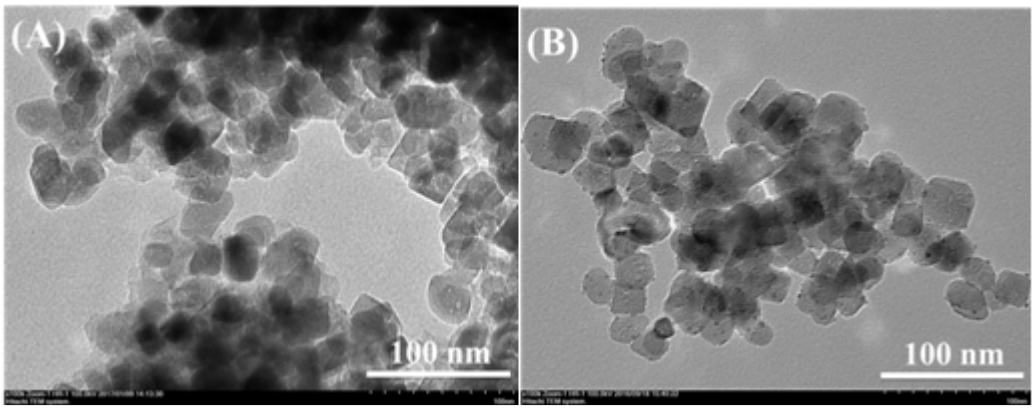


Figure 1 TEM images of pure TiO_2 (A) and PDs-TiO_2 (B)

The figure below shows the photographs of pure Gauze, Gauze-TiO_2 and Gauze-PDs-TiO_2. It can be seen from the figure that the pure Gauze is white and woven loosely, and there are a large number of holes on the surface, making Gauze suitable for immobilizing TiO_2. After immobilizing TiO_2, the Gauze remains white, but its surface is slightly hardened, indicating that PVA is successfully bonded to the surface of Gauze. The color of Gauze-PDs-TiO_2 is brown and the surface of Gauze-PDs-TiO_2 is also slightly hardened, indicating that PDs-TiO_2 has been successfully immobilized on the surface of Gauze.

Figure 2 Photographs of pure Gauze (A), Gauze-TiO2 (B) and Gauze-PDs-TiO2 (C)

The figure below shows the SEM images of pure Gauze and Gauze-PDs-TiO_2. It can be seen from the figure that the pure Gauze is made of flat fibers, which means that the Gauze is pure cotton. There are a lot of wrinkles on the surface of fiber and these wrinkles are advantageous for immobilizing TiO_2. After immobilized the PDs-TiO_2 photocatalyst, a uniform layer of coating can be clearly seen on the surface of the fiber, and the thickness of this covering is less than 5μm. It is noteworthy that some granular aggregates can be clearly seen on the surface of the fiber and the size of these aggregates is about 2-10μm. It is certain that these particles are PDs-TiO_2. Although PDs-TiO_2 particles cannot be dispersed in nanometer scale on the surfaces of fibers, their original particle size is about 20 nm, so Gauze-PDs-TiO_2may have good catalytic activity. Furthermore, the elemental mapping images of Gauze-PDs-TiO_2 (Figure 4) obtained by energy dispersive X-ray (EDX)suggest that C (green), O (red), Ti (blue) elements are distributed throughout the entire sample, so PDs-TiO_2 particles were immobilized on the surface of Gauze successfully.

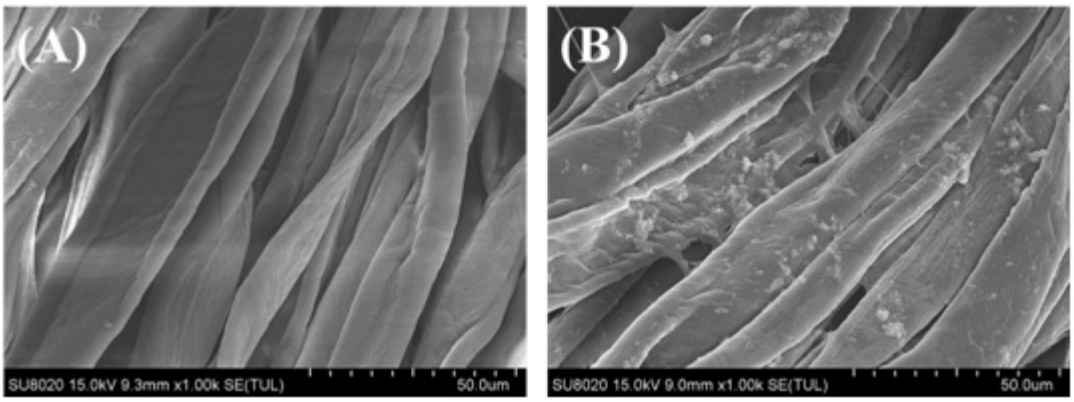


Figure 3 SEM imagines of pure Gauze (A) and Gauze-PDs-TiO2 (B)

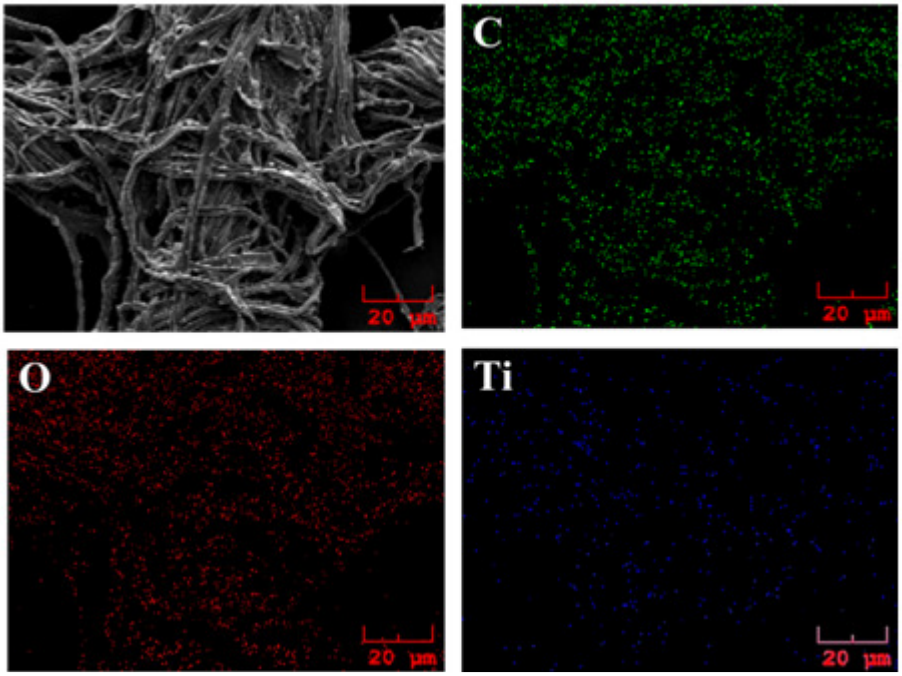


Figure 4 EDX elemental mapping images of Gauze-PDs-TiO_2

In relevant literatures, formaldehyde or glutaraldehyde are commonly used to crosslink PVA. However, formaldehyde and glutaraldehyde have great toxicity and taste. In recent years, the method of thermal crosslink of PVA has attracted much attention [9]. Here, we try to crosslink PVA with thermal crosslinking method. First, the heat resistance of Gauze was characterized by TGA (Figure 5). As shown in the Figure 5, the weight loss of pure Gauze is only about 0.6% at 300 ^{o}C, which is due to the removal of the surface hydroxyl and adsorbed water in the gauze. The thermal crosslinking of PVA is stable at 140^{o}C, so it is feasible to crosslink PVA on the surface of gauze. From the TGA curves of Gauze-TiO_2 and Gauze-PDs-TiO_2, the initial thermal decomposition temperature of Gauze is slightly decreased, which may be caused by the relatively low heat resistance temperature of PVA. In addition, the weight loss of pure Gauze is 100% at above 550 ^{o}C, indicating that it can be completely degraded. Therefore, the residual weight of

Gauze-TiO_2 and Gauze-PDs-TiO_2 at 600 ^oC is the content of TiO_2, so the content of TiO_2 in Gauze-TiO_2 and Gauze-PDs-TiO_2 is about 1.8%.

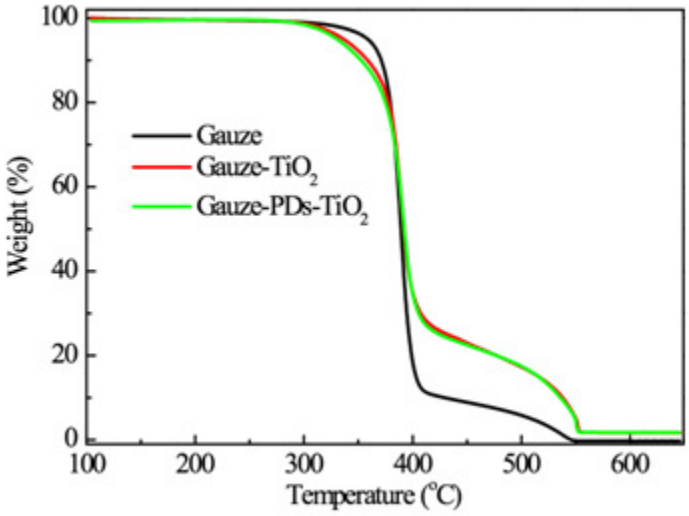


Figure 5 TGA Curves of Pure Gauze, Gauze-TiO2 and Gauze-PDs-TiO2
(in air, 20 oC /min)

Figure 6 shows the FTIR curves of pure Gauze, Gauze-TiO_2 and Gauze-PDs-TiO_2. It can be seen from the figure that the Gauze has obvious absorption peaks at 3,286cm^{-1}, 2,920cm^{-1}, 1,655cm^{-1}, 1,427cm^{-1} and 1,080cm^{-1}, and these absorption peaks correspond to OH stretching vibration, CH_2 stretching vibration, OH bending vibration, CH_2 bending vibration and C-O stretching vibration respectively. This indicates that the Gauze is made of pure cotton. After immobilized TiO_2, the FTIR spectra of Gauze-TiO_2 and Gauze-PDs-TiO_2 are basically the same as that of pure Gauze, indicating that the immobilized process and heat treatment process have no damage to the Gauze.

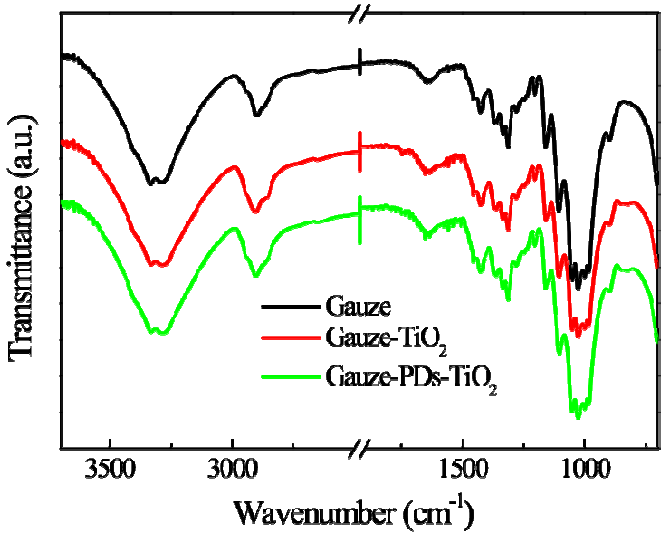


Figure 6 FTIR Curves of Pure Gauze, Gauze-TiO_2 and Gauze-PDs-TiO_2

The photocatalytic activity of Gauze-TiO_2 and Gauze-PDs-TiO_2under visible light irradiation was characterized by using methyl orange as model pollutant. Figure 7 shows the concentration curve of methyl orange under visible light irradiation. The concentration of methyl orange decreased with the progress of irradiation, indicating that both Gauze-TiO_2 and Gauze-PDs-TiO_2 could degrade methyl orange, so TiO_2 was successfully immobilized on the surface of Gauze. After visible light irradiation for 8h, Gauze-TiO_2 degraded about 12% of methyl orange, while Gauze-PDs-TiO_2 degrade about 60% of methyl orange. It's obvious that the degradation rate of Gauze-PDs-TiO_2 was about 5.0 times than that of Gauze-TiO_2, indicating that the polymer dots can absorb visible light and successfully transfer the generated electrons to TiO_2, Moreover, the concentration curve of methyl orange is basically a straight line, indicating that the photocatalytic activity of Gauze-TiO_2 and Gauze-PDs-TiO_2 is stable.

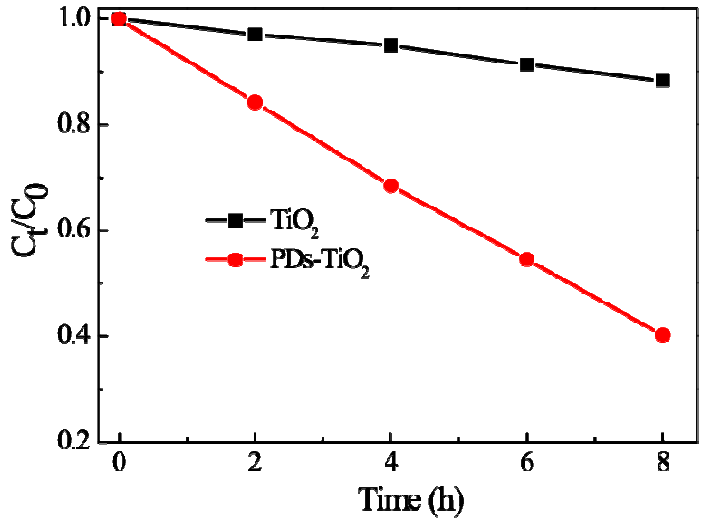


Figure 7 Photocatalytic degradation of Methyl Orange solution under visible light irradiation

4. CONCLUSION

To sum up, TiO_2 and PDs-TiO_2 are successfully immobilized on the surface of Gauze by using thermal crosslinked PVA as the binder. TGA shows that the amount of TiO_2 immobilized on the surface of Gauze is about 1.8%. FTIR shows that the immobilized process and heat treatment process of TiO_2 have no damage on Gauze. Under visible light irradiation, the degradation rate of methyl orange on Gauze-PDs-TiO_2 was about 5 times higher than that onGauze-TiO_2. This novel design of Gauze-PDs-TiO_2 is simple, green and effective, and may open up a new avenue for fabricating high performance visible light photocatalysts and facilitating their practical application.

REFERENCES

[1] J.Mo, Y. Zhang, Q. Xu, J.J. Lamson, R. Zhao, Photocatalytic purification of volatile organic compounds in indoor air: A literature review, Atmospheric Environment, 43 (2009) 2229-2246.

[2] H. Zhang, X. Lv, Y. Li, Y. Wang, J. Li, P25-Graphene Composite as a High Performance Photocatalyst, ACS Nano, 4 (2010) 380-386.

[3] N. Daneshvar, D. Salari, A. Niaei, M.H. Rasoulifard, A.R. Khataee, Immobilization of TiO2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23, Environmental Letters, 40 (2005) 1605-1617.

[4] S. Matsuzawa, C. Maneerat, Y. Hayata, T. Hirakawa, N. Negishi, T. Sano, Immobilization of TiO2 nanoparticles on polymeric substrates by using electrostatic interaction in the aqueous phase, Applied Catalysis B: Environmental, 83 (2008) 39-45.

[5] J. Shang, W. Li, Y. Zhu, Structure and photocatalytic characteristics of TiO2 film photocatalyst coated on stainless steel webnet, Journal of Molecular Catalysis A: Chemical, 202 (2003) 187-195.

[6] J. Zhang, H. Yang, L. Jiang, Y. Dan, Enhanced photo-catalytic activity of the composite of TiO2 and conjugated derivative of polyvinyl alcohol immobilized on cordierite under visible light irradiation, Journal of Energy Chemistry, 25 (2016) 55-61.

[7] S. Hashemizad, M. Montazer, A. Rashidi, Influence of the surface hydrolysis on the functionality of poly(ethylene terephthalate) fabric treated with nanotitanium dioxide, Journal of Applied Polymer Science, 125 (2012) 1176-1184.

[8] K. Qi, J.H.X. †, W.A. Daoud, C.L. Mak, Functionalizing Polyester Fiber with a Self-Cleaning Property Using Anatase TiO 2 and Low-Temperature Plasma Treatment, International Journal of Applied Ceramic Technology, 4 (2007) 554–563.

[9] P. Lei, F. Wang, X. Gao, Y. Ding, S. Zhang, J. Zhao, S. Liu, M. Yang, Immobilization of TiO2 nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants, Journal of hazardous materials, 227-228 (2012) 185-194.

[10] G. Li, F. Wang, P. Liu, Z. Chen, P. Lei, Z. Xu, Z. Li, Y. Ding, S. Zhang, M. Yang, Polymer dots grafted TiO2 nanohybrids as high performance visible light photocatalysts, Chemosphere, 197 (2018) 526-534.