

# Preparation and Photocatalytic Properties of TiO<sub>2</sub> Immobilized on Fiberglass Cloth

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**Abstract**— In this study, the TiO<sub>2</sub> immobilized on fiberglass cloth was prepared to improve the photocatalytic activity of TiO<sub>2</sub> and overcome the difficulty of reuse through a set of different procedures. The microstructure and morphology of TiO<sub>2</sub> loaded on FGC were characterized via SEM and XRD, respectively. The photocatalytic activity of TiO<sub>2</sub>-fiberglass specimens was assessed by the yield of hydroxyl radicals and the extent to which humic acid (HA) was photodegraded in a small reactor. The result revealed that (i)the crystalline structure of immobilized TiO<sub>2</sub> was nearly unchanged compared with pure P25 nanoparticles. (ii)the TiO<sub>2</sub>-fiberglass specimens prepared by PA and HY procedures resulted in more TiO<sub>2</sub> particles loading on FGC and exhibited better photocatalytic activity than by SG procedure. (iii)The steady state concentration of hydroxyl radicals in the photocatalytic system was obtained as  $1.11 \times 10^{-14} \text{ mol.L}^{-1}$ . (iv)The TiO<sub>2</sub>-fiberglass specimens prepared by HY procedure exhibited good photocatalytic activity on HA degradation.

**Keywords**-TiO<sub>2</sub>; Fiberglass Cloth; photocatalytic properties

## I. INTRODUCTION

Due to the ability to oxidize organic molecules at low energy cost, photocatalysis has become a promising technique for the treatment of wastewater containing organic pollutants in recent years[1,2]. In this field, nano-titanium dioxide (TiO<sub>2</sub>) is considered as one of the most promising photocatalyst for environmental remediation due to its physicochemical properties such as thermal and chemical stability, relatively high photocatalytic activity, low-toxicity, and low cost [3-5].

In a typical application for photocatalysis, TiO<sub>2</sub> have commonly been used in a powder form, which leading to the difficulty of post separation of TiO<sub>2</sub> from the suspending system and inevitably causes secondary pollution. This prevents the large-scale application of TiO<sub>2</sub> photocatalysis in water and air remediation [6, 7].

To overcome the separation difficulty, the immobilization of TiO<sub>2</sub> onto solid materials was developed. Among supporting materials (glass beads, perlite granules, zeolite, etc.), Fiberglass cloth (FGC) is economical, flexible, corrosion resistant and easy to handle [8-11]. However, there are fewer studies on the photocatalytic degradation of MCs in a liquid phase using TiO<sub>2</sub> immobilized onto FGC. In this study, the TiO<sub>2</sub> immobilized FGC was introduced which was expected to effectively improve the removal rate of MCs in aqueous phase and deal with the problem of recycle.

## II. EXPERIMENTAL

### A. Preparation of Tio<sub>2</sub> Immobilized on fiberglass Cloth

#### 1) Paste procedure(PA)

The active TiO<sub>2</sub> catalyst was purchased from Degussa. An aqueous TiO<sub>2</sub> particle dispersion (2g in 150ml of deionized water and agitating for 10 minutes) was used as a source of titania. The dispersion was loaded onto the fiberglass cloth using a paintbrush, after which the cloth was dried and calcined in an electric furnace at 200 °C(heat rate, 2 °C min<sup>-1</sup>) for 2 h.

#### 2) Sol-gel procedure (SG)

Tetrabutyl orthotitanate (TBOT) (85ml), triethanolamine (15ml) and ethanol (400ml) were mixed and agitated for 1.5h. A solution of deionized water (9ml) and ethanol (50ml) with a pH value of 3 (adjusted by 1 mol.L<sup>-1</sup> nitric acid) was subsequently added to the above mixture and kept stirring for 1h at ambient temperature. The resultant light yellow and transparent sol was obtained and aged for 24h from light.

#### 3) Hybrid procedure (HY)

The hybrid methods consisted of two steps: in step 1 the TiO<sub>2</sub> was applied onto the fiberglass cloth by the PA procedure; in the subsequent step 2 the resulting specimen was dip-coated into the sol-gel TiO<sub>2</sub> solution twice to cover some of the imperfections left by the PA method in step 1.

Note that after each step the TiO<sub>2</sub> fiberglass specimen was heat-treated at 400 °C for 2h (heat rate, 2 °C min<sup>-1</sup>).

### B. Photocatalytic Degradation Experiments

The photocatalytic activity of the TiO<sub>2</sub> specimens prepared by different procedures were assessed by the yield of hydroxyl radicals and the extent to which humic acid (HA) was photodegraded in a small reactor.

A 30 W low pressure UV lamp with maximal light intensity at 365 nm was used as the light source for photocatalytic reaction. Salicylic acid was applied as molecular probe to determine the yield of hydroxyl radicals in TiO<sub>2</sub>-FGC photocatalytic system[1]. The prepared TiO<sub>2</sub>-fiberglass specimens were immersed in the 500 mL salicylic acid solution (150 mg.L<sup>-1</sup>, pH=6.0) and stirred constantly for 60min. The temporal concentration of dihydroxy benzoic acid, the main photodegradation products of salicylic acid, was measured to infer the yield of hydroxyl radicals by the followed equation[12]:

$$[\bullet\text{OH}]_{ss} = K_e / K_b \quad (1)$$

Where  $[\bullet\text{OH}]_{ss}$ ,  $K_e$  and  $K_b$  were the steady state concentration of hydroxyl radicals, the pseudo first order reaction rate constant and the second order reaction rate constant, respectively.

In the HA photodegradation experiment, TiO<sub>2</sub>-fiberglass specimens were submerged in the 500 mL HA solution (10 mg.L<sup>-1</sup>, pH=6.5) and kept stirring for 2h under the irradiation of UV lamp. The variation of HA concentration was detected to evaluate the photocatalytic performance of prepared TiO<sub>2</sub>-fiberglass specimens.

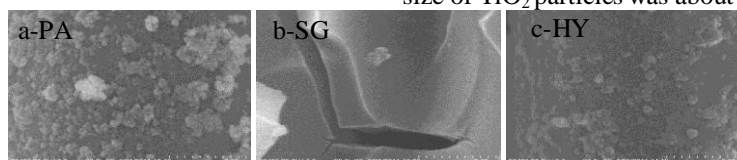


Figure 1. SEM images of TiO<sub>2</sub> loading on FGC by different procedures (a-PA, b-SG, c-HY)

### 2) X-ray diffraction (XRD)

The XRD patterns of commercial titanium dioxide (P25) and TiO<sub>2</sub> immobilized on FGC by HY procedure were presented in Fig. 2. Clearly, both materials exhibit the similar XRD patterns. As shown in Fig.2, the series of strong peaks at 2θ of 25.2, 37.8 and 38.5 were respectively corresponding to the (101), (004) and (112) crystal planes of anatase phase, and the peak at 2θ of 27.4 was corresponding to the (110) crystal plane of rutile phase as well. These signals were indicative of the dominant anatase phase in both catalysts which was generally recognized with higher photocatalytic activity than rutile form.

According to the Scherrer formula[13], the mean particles of P25 and TiO<sub>2</sub> loaded on FGC were respectively calculated to be 21nm and 16nm, which was in concordance with the results of SEM. The results indicated the catalysts immobilized on FGC had larger specific surface area than that of P25 which was conducive to photocatalytic performance.

### C. Materials and Analytical Measurements

The fiberglass cloth was provided by Shanghai Yaohong Glass Fiber Co., Ltd. (thickness: 0.26mm; weight: 280 g m<sup>-2</sup>), and is the same fabric used in the manufacturing of fiberglass-reinforced plastics (insulation materials). The salicylic acid and humic acid were supplied by Sinopharm Chemical Reagent Co., Ltd. The UV lamp was bought from the Beijing NBeT Group Co., Ltd.

Scanning electron micrographs (SEM) of the TiO<sub>2</sub>-fiberglass cloth specimens were taken with a Hitachi 3400N electron microscope. The crystalline forms of TiO<sub>2</sub> (anatase and/or rutile) were assessed by XRD measurements using an ARL XTRA/3KW X-ray diffractometer. The temporal concentration of dihydroxy benzoic acid and HA were monitored by UV-7504 UV/Vis spectrophotometer from Shanghai Precision Instrument Co., Ltd.

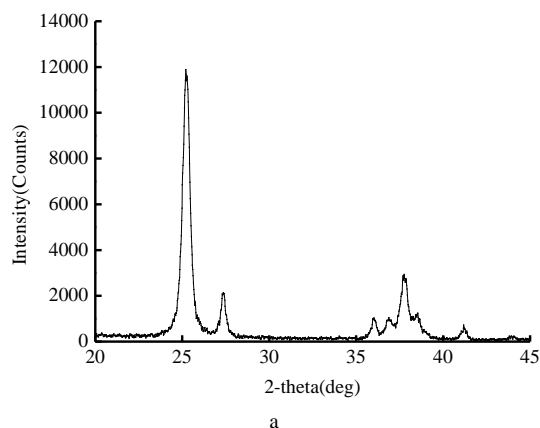
## III. RESULTS AND DISCUSSION

### A. Characterization

#### 1) Scanning electron microscopy (SEM)

Fig.1 were the SEM images of TiO<sub>2</sub> loaded on FGC by three procedures. It was apparently that only a small amount of TiO<sub>2</sub> nanoparticles were immobilized on the FGC by SG procedure, and the patterns of PA and HY resulted in more TiO<sub>2</sub> particles loading on FGC compared to the pattern of SG, which indicated the PA procedure was more effectively way to immobilize TiO<sub>2</sub> onto FGC than SG.

As showed in all images, the TiO<sub>2</sub> nanoparticles distributed evenly on the FGC with regular and orderly structure. According to the TEM image, the average particle size of TiO<sub>2</sub> particles was about 15 nm.



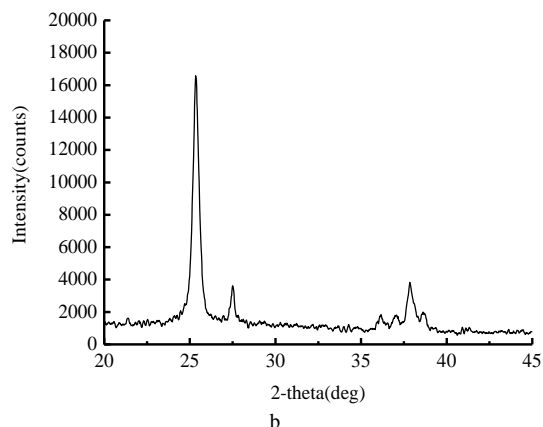


Figure 2. XRD patterns of P25(a) and  $\text{TiO}_2$  immobilized on FGC by HA1 procedure(b)

### B. Photocatalytic Performance of $\text{TiO}_2$ Immobilized on FGC

#### 1) Photocatalytic activity evaluation of $\text{TiO}_2$ -FGC specimens

Fig. 3 showed the temporal concentration of dihydroxy benzoic acid in 150 min by  $\text{TiO}_2$  -FGC photocatalytic system. It exhibited the absorbance increased with the irradiation time extended. After 60 minutes reaction the absorbance rose slowly and tended stable. According the equation described in section 2.2, the pseudo first order reaction rate ( $K_e$ ) was gained as about  $0.018 \text{ min}^{-1}$  by using linear regression. The second order reaction rate constant ( $K_b$ ) had been reported as  $2.7 \times 10^{10} \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$  [14]. So the steady state concentration of hydroxyl radicals ( $[\cdot\text{OH}]_{ss}$ ) in the photocatalytic system could be obtained as  $1.11 \times 10^{-14} \text{ mol} \cdot \text{L}^{-1}$ . Ren et al. had reported the steady state concentration of hydroxyl radicals as  $1.68 \times 10^{-14} \text{ mol} \cdot \text{L}^{-1}$  at the optimal experimental conditions which the initial concentration of salicylic acid was  $50 \text{ mg} \cdot \text{L}^{-1}$  and the illuminant was 500 w medium pressure mercury lamp [15]. The different of results may be attributed to the difference of light intensity. The yield of hydroxyl radicals was in proportion to the light intensity under certain quantum yield condition.

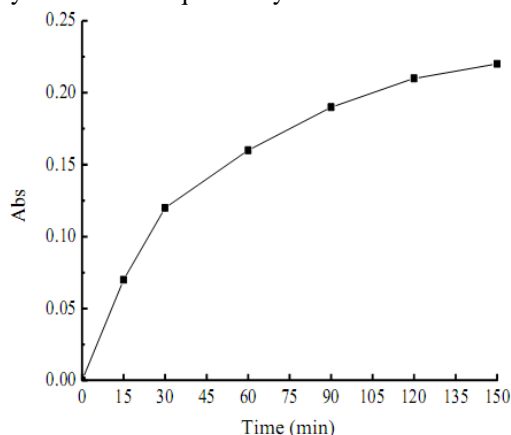


Figure 3. The temporal concentration of dihydroxy benzoic acid in  $\text{TiO}_2$ -fiberglass photocatalytic system

#### 2) Photocatalytic degradation of HA by $\text{TiO}_2$ -FGC system

Fig. 4 presented the temporal loss of HA during photodegradation process by  $\text{TiO}_2$  -FGC system. According the result of section 3.1.1, the  $\text{TiO}_2$ -fiberglass specimen prepared by HY procedure was applied in this experiment. As can be seen in Fig. 4, about 70% of HA was removed in 120 minutes illumination which proved the  $\text{TiO}_2$ -FGC system have potential application in water pollutants removal.

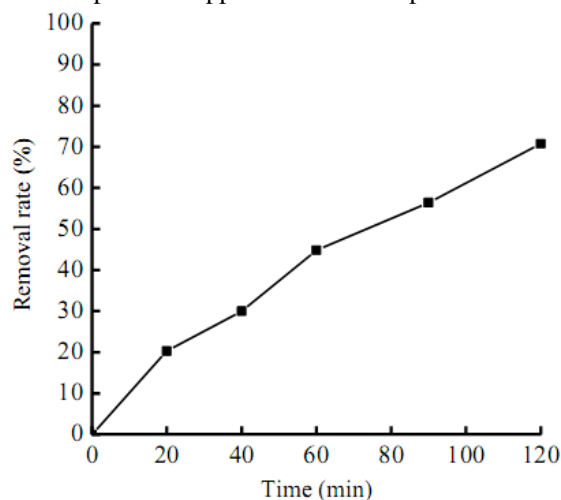


Figure 4. The photodegradation of humid acid in solution by  $\text{TiO}_2$ -fiberglass

### IV. CONCLUSION

The active  $\text{TiO}_2$  particles were immobilized onto a fiberglass support by various preparative procedures (paste, sol-gel and hybrid procedures) to yield catalytically active systems for organic pollutants removal in water environment and deal with the problem of recycle. The characterization of SEM and XRD showed the crystalline structure of immobilized  $\text{TiO}_2$  was nearly unchanged compared with pure P25 nanoparticles and the PA procedure was more effectively way to immobilize  $\text{TiO}_2$  onto FGC than SG. The steady state concentration of hydroxyl radicals ( $[\cdot\text{OH}]_{ss}$ ) in the photocatalytic system was obtained as  $1.11 \times 10^{-14} \text{ mol} \cdot \text{L}^{-1}$  by using salicylic acid as the molecular probe. The  $\text{TiO}_2$ -fiberglass specimens prepared by HY procedure exhibited good photocatalytic activity on HA degradation.

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### REFERENCES

- [1] Phuong T.N. Nguyena, b., Chris S., Winarto K., Hirofumi H., A non-hydrolytic sol-gel synthesis of reduced graphene oxide/ $\text{TiO}_2$  microsphere photocatalysts. *Catalysis Today*, 230, pp.166-173(2014).
- [2] Jérôme L. C., Vesna T., Ozren W., Photocatalytic degradation of the herbicide terbuthylazine: Preparation, characterization and

- photoactivity of the immobilized thin layer of  $\text{TiO}_2$ /chitosan. *Journal of Photochemistry and Photobiology A: Chemistry*, 309, pp.22–29(2015).
- [3] Mor GK, Prakasam HE, Varghese OK, Shankar K, Grimes CA., Vertically oriented Ti-Fe-O nanotube array films: Toward a useful material architecture for solar spectrum water photoelectrolysis. *Nano. Lett.*, 7, pp. 2356–2364(2007).
- [4] Chiarello GL, Selli E, Forni L., Photocatalytic hydrogen production over flame spray pyrolysis-synthesised  $\text{TiO}_2$  and Au/ $\text{TiO}_2$ . *Appl. Catal. B Environ.*, 84, pp. 332–339(2008).
- [5] Seger B, Kamat PV., Fuel cell geared in reverse: photocatalytic hydrogen production using a  $\text{TiO}_2$ /Nafion/Pt membrane assembly with no applied bias. *J. Phys. Chem. C*, 113, pp. 18946–18952(2009).
- [6] Chen X., Mao S.S., Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.* 107, pp. 2891–2959(2007).
- [7] Burda C., Chen X., Narayanan R., El-Sayed M.A., Chemistry and properties of nanocrystals of different shapes, *Chem. Rev.* 105, pp. 1025–1102(2005).
- [8] Shen C., Wang Y.J., , Xu J.H., Luo G.S., Facile synthesis and photocatalytic properties of  $\text{TiO}_2$  nanoparticles supported on porous glass beads. *Chemical Engineering Journal*, 209, pp.478–485(2012).
- [9] Shavisia Y., Sharifniaa, S., Hosseinib S.N., Khadivia M.A., Application of  $\text{TiO}_2$ /perlite photocatalysis for degradation of ammonia in wastewater. *Journal of Industrial and Engineering Chemistry*, 1(20), pp.278–283(2014).
- [10] Wang C., Li Y., Shi, H. S., Huang, J. F., Preparation and characterization of natural zeolite supported nano  $\text{TiO}_2$  photocatalysts by a modified electrostatic self-assembly method. *Surface and Interface Analysis*, 1(47), pp.142–147(2015).
- [11] Valtierra J.M., Servín J.G., Reyes C.F., Calixto S., The photocatalytic application and regeneration of anatase thin films with embedded commercial  $\text{TiO}_2$  particles deposited on glass microrods, *Appl. Surf. Sci.* 252, pp.3600–3608(2006).
- [12] Hideki K., Steady-state concentrations of hydroxyl radical in titanium dioxide aqueous suspensions. *Chemosphere*, 22(11), pp:1003–1009(1991).
- [13] Spurr R. A., Myers H., Quantitative analysis of anatase-rutile mixtures with an X-Ray diffractometer. *Anal. Chem.*, 29 (5), pp.760–762(1957).
- [14] George V B, Clive L G, Alberta B R., Critical review of rate constants for reactions of hydrated electrons hydrogen atoms and hydroxyl radical( $\bullet\text{OH}/\bullet\text{O}^\cdot$ ) in aqueous solution. *Physical Chemistry Reference Data*, 17 (2), pp.513 – 886(1988).
- [15] Ren X. C., Shi Z. F., Kong L R., et al., Salicylic acid as a molecular probe to determine hydroxyl free radicals in a  $\text{TiO}_2$  thin films photocatalytic system. *Acta Scientiae Circumstantiae*, 28(4), pp.705–709(2008). (in Chinese)