Preparation and Photocatalytic Properties of TiO$_2$ Immobilized on Fiberglass Cloth

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Abstract—In this study, the TiO$_2$ immobilized on fiberglass cloth was prepared to improve the photocatalytic activity of TiO$_2$ and overcome the difficulty of reuse through a set of different procedures. The microstructure and morphology of TiO$_2$ loaded on FGC were characterized via SEM and XRD, respectively. The photocatalytic activity of TiO$_2$-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$_2$ was nearly unchanged compared with pure P25 nanoparticles. (ii) the TiO$_2$-fiberglass specimens prepared by PA and HY procedures resulted in more TiO$_2$ 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 1.11×10$^{-11}$ mol.L$^{-1}$. (iv) The TiO$_2$-fiberglass specimens prepared by HY procedure exhibited good photocatalytic activity on HA degradation.

Keywords—TiO$_2$; 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$_2$) 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$_2$ have commonly been used in a powder form, which leading to the difficulty of post separation of TiO$_2$ from the suspending system and inevitably causes secondary pollution. This prevents the large-scale application of TiO$_2$ photocatalysis in water and air remediation [6, 7].

II. EXPERIMENTAL

A. Preparation of TiO$_2$ Immobilized on fiberglass Cloth

1) Paste procedure (PA)

The active TiO$_2$ catalyst was purchased from Degussa. An aqueous TiO$_2$ 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$^{-1}$) 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$^{-1}$ 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$_2$ was applied onto the fiberglass cloth by the PA procedure; in the subsequent step 2 the resulting specimens were dip-coated into the sol–gel TiO$_2$ solution twice to cover some of the imperfections left by the PA method in step 1.
Note that after each step the TiO2 fiberglass specimen was heat-treated at 400 °C for 2h (heat rate, 2°C min⁻¹).

B. Photocatalytic Degradation Experiments

The photocatalytic activity of the TiO2 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 a molecular probe to determine the yield of hydroxyl radicals in TiO2-FGC photocatalytic system. The prepared TiO2-fiberglass specimens were immersed in the 500 mL salicylic acid solution (150 mg.L⁻¹, pH=6.0) and stirred constantly for 60min. The temporal concentration of dihydroxy benzoic acid and HA were monitored by UV-7504 UV/Vis spectrophotometer from Shanghai Precision Instrument Co., Ltd. The UV lamp was bought from the Beijing NBeT Group Co., Ltd.

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 TiO2-fiberglass cloth specimens were taken with a Hitachi 3400N electron microscope. The crystalline forms of TiO2 (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 TiO2 loaded on FGC by three procedures. It was apparently that only a small amount of TiO2 nanoparticles were immobilized on the FGC by SG procedure, and the patterns of PA and HY resulted in more TiO2 particles loading on FGC compared to the pattern of SG, which indicated the PA procedure was more effectively way to immobilize TiO2 onto FGC than SG.

As showed in all images, the TiO2 nanoparticles distributed evenly on the FGC with regular and orderly structure. According to the TEM image, the average particle size of TiO2 particles was about 15 nm.

2) X-ray diffraction (XRD)

The XRD patterns of commercial titanium dioxide (P25) and TiO2 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 20 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 20 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 TiO2 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⁻²), and is the same fabric used in the manufacturing of fiberglass-reinforced plastics (insulation materials). The XRD patterns of commercial titanium dioxide (P25) and TiO2 immobilized on FGC by HY procedure were respectively corresponding to the (101), (004) and (112) crystal planes of anatase phase, and the peak at 20 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.

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B. Photocatalytic Performance of TiO\textsubscript{2} Immobilized on FGC

1) Photocatalytic activity evaluation of TiO\textsubscript{2} –FGC specimens

Fig. 3 showed the temporal concentration of dihydroxy benzoic acid in 150 min by TiO\textsubscript{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 min\textsuperscript{-1} by using linear regression. The second order reaction rate constant ($K_b$) had been reported as 2.7 $\times$ 10\textsuperscript{-10} mol\textsuperscript{-1}.L.s\textsuperscript{-1}[14]. So the steady state concentration of hydroxyl radicals ([•OH]\textsubscript{ss}) in the photocatalytic system could be obtained as 1.11 $\times$ 10\textsuperscript{-14} mol.L\textsuperscript{-1}. Ren et al. had reported the steady state concentration of hydroxyl radicals as1.68$\times$10\textsuperscript{-14} mol.L\textsuperscript{-1} at the optimal experimental conditions which the initial concentration of salicylic acid was 50 mg. 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.

2) Photocatalytic degradation of HA by TiO\textsubscript{2} -FGC system

Fig. 4 presented the temporal loss of HA during photodegradation process by TiO\textsubscript{2} -FGC system. According the result of section 3.1.1, the TiO\textsubscript{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 TiO\textsubscript{2}-FGC system have potential application in water pollutants removal.

IV. CONCLUSION

The active TiO\textsubscript{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 TiO\textsubscript{2} was nearly unchanged compared with pure P25 nanoparticles and the PA procedure was more effectively way to immobilize TiO\textsubscript{2} onto FGC than SG. The steady state concentration of hydroxyl radicals ([•OH]\textsubscript{ss}) in the photocatalytic system was obtained as 1.11 $\times$ 10\textsuperscript{-14} mol.L\textsuperscript{-1} by using salicylic acid as the molecular probe. The TiO\textsubscript{2}-fiberglass specimens prepared by HY procedure exhibited good photocatalytic activity on HA degradation.

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