PHOTOCATALYTIC OXIDATION OF ACETALDEHYDE BY MODIFIED CARBON NANOFIBERS

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1 Introduction

TiO_2 photocatalysis has been extensively studied with regard to its application in environmental remediation processes [1]. The photocatalytic reactions are initiated by the absorption of UV photons with the concurrent gerenration of conduction band electrons and valence band holes in the TiO_2 lattices. The remediation power of TiO_2 photocatalysts can be largely attributed to the strong oxidation potential of these OH radicals, which are produced from the reaction between the valence band holes and surface hydroxyl groups.

Fir air purification, immobilized photocatalysts on support materials are usually employed. Generally, the surface area and the activities are reduced by the immobilization of photocatalysts. Therefore, support materials with high surface areas have been applied to immobilize photocatalysts. Activated carbon has a high surface are, which is closely related to the enhancement of adsorption and photocatalytic activities.

Recently, some researchers have recently reported that carbon nanofibers could be prepared by electrospinning methods [2]. Electrospinning technique is a simple method for making ultra thin fibers from various polymer solutions. Moreover, nanoparticles can be directly added to the solution used for electrospinning in order to obtain nanofibers. Therefore, using the electrospinning techniques, photocatalysts may be easily embedded into carbon nanofibers. Previously, we prepared TiO_2 embedded carbon nanofibers by electrospinning method. TiO_2 embedded carbon nanofibers are efficiently degraded the gaseous acetaldehyde under UV irradiation [3].

Noble metals, such as Pt, Ag, and Au, were easily deposited on photocatalysts by the photodeposition method and the surface fluorinated TiO_2 was simply prepared by NaF addition at acidic pH. Surface modifications such as noble metal deposition and surface fluorination could be enhancing the photocatalytic oxidation.

In this study, we have prepared TiO_2 embedded polyacrylonitrile (TiO_2/PAN) fibers. Subsequent calcinations of TiO_2/PAN under N_2 atmosphere produced TiO_x embedded carbon nanofibers (TiO_x/CNF). Finally, thermal treatment of the TiO_x/CNF under air conditions resulted in oxidized TiO_x/CNF (TiO_2-CNF). The effects of the amount of TiO_2 and the surface modification of TiO_2-CNF have been studied.

2 Experimental

2.1 Preparation of Composite Fibers

A 10wt.% solution of PAN in DMF was prepared. TiO_2 powder was dispersed in this PAN/DMF solution. The yellowish viscous TiO_2/PAN gel was placed in a hypodermic syringe, which was positioned at a fixed distance from a metal cathode as a collector. Dense webs of nanofibers were collected under an applied potenticial of 20 kV. For the preparation of TiO_2-CNF, the TiO_2/PAN was placed in a tube furnace and then carbonized under N_2 atmosphere. Finally, TiO_x/CNF was calcined for 3h at 400 ^oC in air, which resulted in its oxidation to TiO_2-CNF. For surface modification, the Au or Pt was deposited on TiO_2-CNF by photodeposition method [4]. Fluorinated TiO_2-CNF was prepared by NaF addition [5].

2.2 Photocatalysis

The photocatalytic oxidation of CH_3CHO was carried out in a closed-circulation reactor under

ambient conditions as described elsewhere [3]. The photocatalytic oxidation of CH_3CHO was carried out in a closed circulation reactor under ambient conditions. Gases used were CH_3CHO (300 ppmv in N_2) as a CH_3CHO standard, O_2 and air as carrier gas. The mixed gas passed through the reservoir and the concentration of CH_3CHO in the exit stream was monitored until it attained a constant value and the gas was then circulated by means of the pump. The circulated gas was passed through a stainless steel reactor with a quartz window so that it came into contact with the surface of a sample placed in a stainless steel reactor. After adsorption equilibrium with the surface of the sample had been established in the dark, the sample was illuminated with UV light.

The removal of CH_3CHO and the production of CO_2 were monitored using a gas chromatograph that was equipped with a Polarpak-Q column, a flame ionization detector, a CO_2 methanizer, and a gas-sampling valve.

The surface morphological images of the composite fibers were obtained by using a FE-SEM. The weight loss of a sample as a function of temperature was monitored by Thermal gravity analysis (TGA) and XRD pattern was obtained with an X-ray diffractometer using Cu Kα1 radiation.

3 Results and Discussion

3.1 Modified Carbon Nanofiber

Fig.1 shows the thermal behaviors of the TiO_2-CNF. The weight loss was decreased with increasing the amount of TiO_2 added and the carbon was oxidized to carbon dioxide above at 570 ^oC. The increase of weight was observed at around 500 ^oC, which might be attributed to the oxidation of TiO_2 from the reaction between TiO_x and atmospheric O_2.

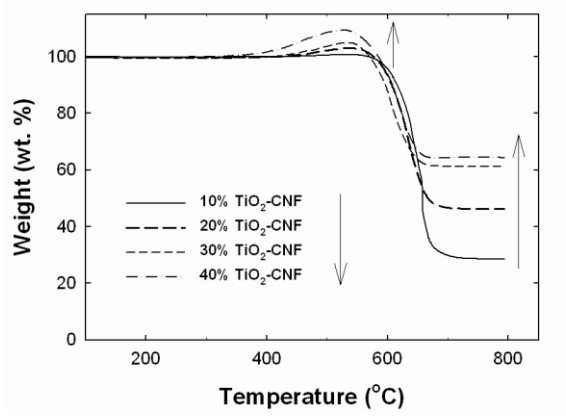

Fig. 1 TGA curves of TiO_2 embedded Carbon nanofibers as a function of the amount of TiO_2

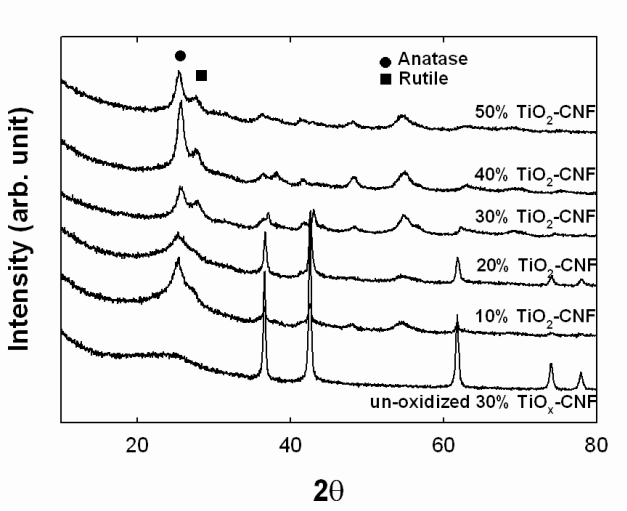

Fig. 2 XRD patterns for TiO_x-CNF and TiO_2-CNF.

Fig. 2 shows the XRD spectra of various fiber samples as a function of the amount of TiO_2. Before oxidation (un-oxidized 30 % TiO_x-CNF), almost all of the anatase pahse had disappeared. This seems to be due to the reduction of TiO_2 during carbonization under an N_2 atmosphere, which might be attributed to a carbothermal reduction process. However, the anatase phase was observed in oxidized TiO_2-CNFs, which implies that the reduced TiO_x was oxidized by the thermal treatment in air. This result might be closely related to the photocatalytic degradation of CH_3CHO. The carbon fibers could be thermally activated during the post oxidation process.

3.2 Photocatalytic Oxidation of Acetaldehyde

Fig. 3 shows the photocatalytic oxidation of CH_3CHO on TiO_2-CNFs by the UV illumination. Before UV irradiation, CH_3CHO was pre-contacted with the sample for 15 min. Direct photolytic degradation of CH_3CHO was not observed at all. With un-oxidized 30 % TiO_x-CNF, the concentration of CH_3CHO did not decrease at all. The anatase phase formation during thermal treatment should be responsible for photocatalytic degradation of CH_3CHO. The photocatalytic degradation rate was optimized on 30 % TiO_2-CNFs.

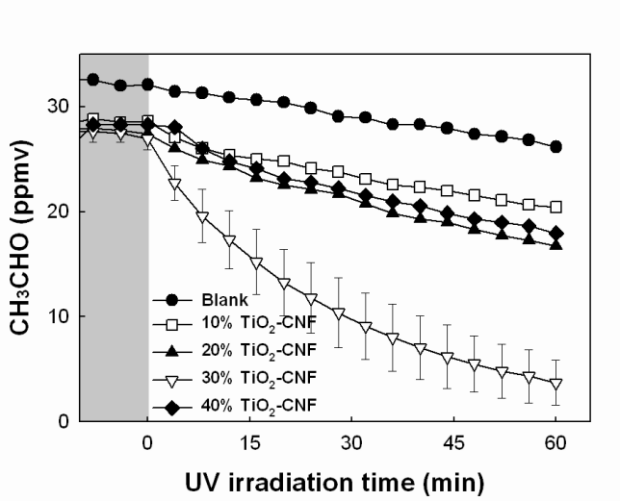

Fig. 3 Photocatalytic degradation of CH_3CHO on TiO_2/CNF as a function of the amount of TiO_2.

This was not consistent with the amounts of anatase phase as shown in Fig. 2. Therefore, the carbon nanofiber as a support might be played an important role.

In order to increase the efficiency of photocatalytic oxidation of CH_3CHO, the surface of 30 % TiO_2-CNF composites was modified by noble metal deposition or surface fluorination. As an effort to increase the photocatalytic activities, noble metal deposition such as Pt or Au on TiO_2 has been a frequent topic of many photocatalytic studies on pollutant degradation. Pt or Au nanoparticle on TiO_2 has been known to act as a kind of electron reservoir and thus pulls the electron from TiO_2 conduction band via the Mott-Schottky interface. Therefore, the photocatalytic degradation rate of organic pollutants should be increased by noble metal deposition due to the efficient charge separation/transfer, which worked as a limiting factor. On the other hand, the surface fluorination is known to replace the surface hydroxyl groups with Ti-F species and significantly changes the photocatalytic reactivity of TiO_2. The enhancement effect was mainly related to the reaction of homogeneous free OH radicals whose formation was favored on fluorinated TiO_2.

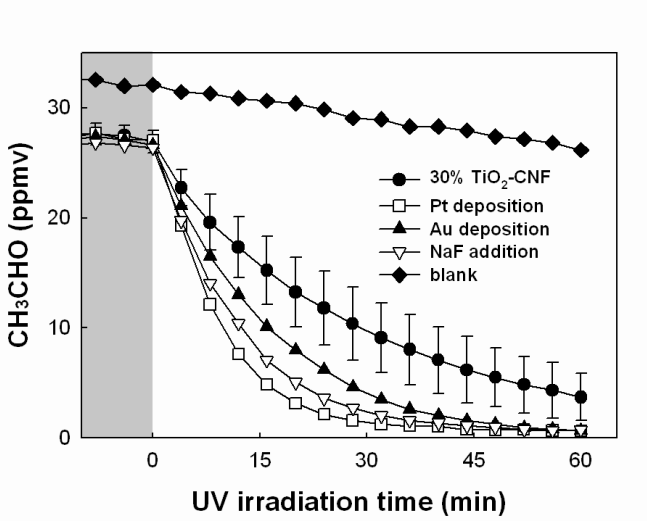

Fig. 4 Photocatalytic degradation of CH_3CHO on modified TiO_2/CNFs.

Fig. 4 shows the surface modification such as Pt or Au deposition and NaF addition could enhance the photocatalytic degradation of CH_3CHO. Pt deposited TiO_2-CNF composites displayed the highest photocatalytic activity. CO_2 was concomitantly produced as a result of CH_3CHO degradation. This result indicates that the surface modification of TiO_2-CNF composites could enhance the photocatalytic activities for the organic pollutant degradation.

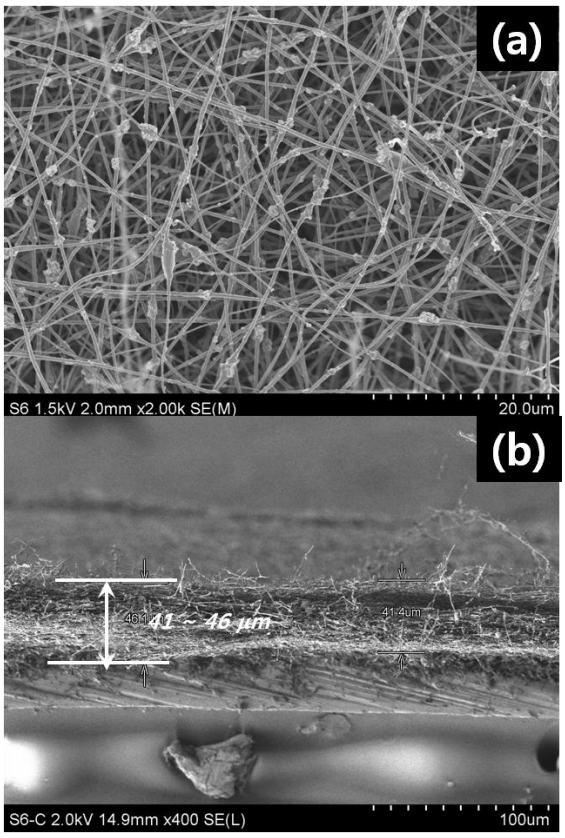

Fig. 5 SEM images of 30 % TiO_2-CNFs.

Fig. 5 shows the SEM image of 30 % TiO_2-CNF. It could clearly be seen that the TiO_2 particles are randomly embedded in the fibers. The thickness of TiO_2-CNF was about 41 ~ 46 μm.
TiO_2-CNF composites were more stable and more flexible than conventional photocatalyst-coated filter. Therefore, this study could be contributed to develop the materials for effective air pollution control.

3 Conclusions

This study exhibited the preparation method for the TiO_2-embedded carbon nanofiber composites but also the simple modification method for effective photocatalytic degradation of CH_3CHO. The photocatalytic degradation rate of CH_3CHO was affected by the amount of TiO_2 and optimized on 30 % TiO_2-CNFs. The surface modification such as Pt or Au deposition and NaF addition could enhance the photocatalytic degradation of gaseous CH_3CHO.

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