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Preparation of carbon/TiO_2 microsphere composites from cellulose/TiO_2 microsphere composites and their evaluation

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Abstract

Cellulose/TiO_2 microsphere composites were made by a one-step phase separation method using cellulose xantate aqueous solution and sodium polyacrylate aqueous solution. The distribution of TiO_2 particles is easily adjusted by adding polyethylene glycol as a diluent. As a result, we succeeded in preparing cellulose/TiO_2 microsphere composites with the surface covered with dense arrangement of TiO_2 by this technique. In addition, carbon/TiO_2 microsphere composites, prepared by carbonization of the cellulose/TiO_2 microsphere composites, were also developed and used as a photocatalyst. The TiO_2 crystal phase in the cellulose/TiO_2 microsphere composites and the microsphere composites, carbonized in a stream of nitrogen at 600 °C, were both found to have the anatase-form as revealed by X-ray diffraction. The process of carbonization proceeded TiO_2 particles appeared more on the surface. The TiO_2 content in the adsorbent was found to be much more than that in commercially activated carbon/TiO_2 composites, as confirmed by elemental analysis. As a result, the carbon surface worked well as the effective to concentrate organic pollutant around the TiO_2 anchored on the composite surface.

Keywords: Cellulose; Titanium dioxide; Carbon/TiO_2 hybrid; Photoassisted catalysis; Acetaldehyde

1. Introduction

Recent environmental applications of photocatalysis have reported on photocatalysts, e.g. titanium dioxide (TiO_2), which have the ability to decompose many kinds of contaminants [1–4]. Minero et al. examined the effect of the addition of Al_2O_3 and SiO_2 as inert supports to the TiO_2 photocatalyst suspension for the photo decomposition of several kinds of organic compounds [5]. To obtain high activated titanium dioxide-composite, they must be heated after anchoring on a support by hydrolysis of $Ti(OR)_4$ (R = alkyl). They observed, however, that the decomposition rates were little affected by the location of the organic compounds, whether in solution, on the photocatalyst or on these inert supports. Ibusuki and Takeuchi used activated carbon as the support for TiO_2 in order to concentrate the organic compounds around the

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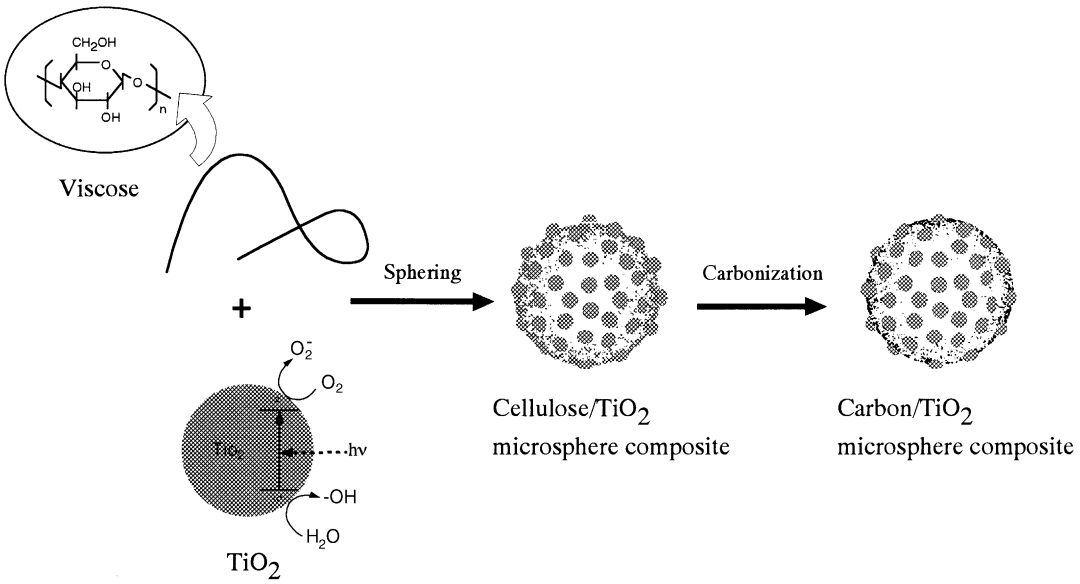

Fig. 1. Schematic illustration of preparation of carbon/TiO_2 microsphere composites.

loaded TiO_2 photocatalysts [6]. They must be also heated after anchoring on a support by hydrolysis of $Ti(OR)_4$ (R = alkyl). However, the shapes and particle sizes of the activated carbon were uneven. Iimura et al. immobilized ZnO to activated carbon by an electroplating method [7], while Matsumoto et al. deposited TiO_2 onto an alumite surface by electroplating [8].

In order to concentrate more organic compounds on the support, we have developed a carbon microsphere doped selectively with TiO_2 nano-particles onto the surface. Active TiO_2 particles could be revealed on the surface of the cellulose microsphere by a one-step phase separation method using cellulose xantate aqueous solution and sodium polyacrylate aqueous solution.

On the other hand, in 1994, we developed a spherical carbon microsphere which could be prepared from the cellulose microsphere for high-performance liquid chromatography (HPLC) [9–11]. Carbon/TiO_2 microsphere composites, prepared from cellulose/TiO_2 microsphere composites by the same method as the spherical carbon packing from cellulose microspheres for HPLC, were also developed and examined as the photocatalyst (Fig. 1).

2. Experimental

2.1. Preparation of carbon/TiO_2 microsphere composites

Cellulose/TiO_2 microsphere composites were made by a one-step phase separation method using cellulose xantate aqueous solution and sodium polyacrylate aqueous solution. TiO_2 powder (P-25, Degussa Co. Ltd., average particle size of 20 nm) was slowly dispersed with the cellulose xantate aqueous solution. The solution was mixed with an aqueous solution containing sodium polyacrylate, and suspended by stirring at 80 °C for 1 h. After heating and congealing, the cellulose/TiO_2 microsphere composites were washed with hydrochloric acid aqueous solution and water.

In addition, carbon/TiO_2 microsphere composites were prepared by carbonization of the cellulose/TiO_2 microsphere composites. To prevent any conglutination among the microspheres due to adsorbed water and coal tar, carbonization was carried out by the following four processes: (1) freeze-drying process; (2) removal of adsorbed water — removal of adsorbed water from cellulose/TiO_2 microsphere composites was carried out by heating at 200 °C in vacuo for

Table 1
Powder characteristics of catalysis samples

Sample	Diameter	Specific surface area (m^2/g)	TiO_2 (%)	C (%)
TiO_2 (P-25)	20 nm[a]	46.5	–	–
TiO_2 (ST-01)	7 nm[a]	258	–	–
Carbon/TiO_2 microsphere composite	25 μm	0.70	41.5	51.5
Cellulose/TiO_2 microsphere composite	45 μm	1.27	15.6	15.6
Carbon microsphere	25 μm	0.58	–	–
Activated carbon TiO_2	–	880	3.5	89.3

[a] The value in the manufacture's literatures.

5 h; (3) dehydration—the microspheres were dehydrated in a stream of dried air for 6 h at 300 °C; and (4) carbonization—the carbonized microspheres were heated to 600 °C for over 5 h and then allowed to stand for 4 h.

Carbon microspheres as reference materials were also prepared using the above-mentioned four processes.

2.2. Charaterization of the structure

Surface area analysis of the particles was carried out by the Brunau-Emmet Teller (BET) method using Autosorb-1 (Aionics Co. Ltd.). Scanning electron micrographs of the microsphere composite were obtained using a Hitachi S-4000 scanning electron micrograph. X-ray diffraction was carried out using a Geiger flex RAD-IIA. The TiO_2 particles of the cellulose/TiO_2 microspheres were determined using electron probe micro analysis (JEOL JXA-8900 WD/ED). The particle size distribution was determined using a laser micron sizer (LMS-30, SEISIN ENTERPRISE Co. Ltd.). For the purpose of comparison of structure analysis of the microsphere composites, activated carbon/TiO_2 composite granules were purchased from Mitsubishi Chemical Corporation.

2.3. Evaluation of the photocatalysis

The catalytic decomposition of acetaldehyde was carried out using a quartz glass cell. Abbreviated in Table 1, a given amount of the photocatalyst powder (cellulose/TiO_2 microsphere, carbon/TiO_2 microsphere composites, naked TiO_2 (P-25, Degussa Co. Ltd., average particle size of 20 nm and ST-01, Ishihara Sangyo Ltd., average particle size of 7 nm) and naked carbon microspheres (average particle size of 25 μm, prepared from cellulose microsphere) was suspended in 3 cm^3 of air-saturated aqueous solution containing 2000 ppm acetaldehyde. The cell was illuminated with two 4 W black lights (TOSHIBA FL4BLB-A: wavelength: 300–400 nm). After a given time of illumination, the photocatalyst was removed by filtering off the suspension of the photocatalyst with a 0.45 μm pore size membrane filter. The filtrate was monitored by measuring the optical absorbance of the filtrates with chromatographs including a Waters 996 photodiode array, Waters 600 pump, Waters 410 differential refractometer and Waters 600 controller with millenium Ver. 2.10J Chromatography manager. A 20 μl portion of the filtrate was injected through a Rheodyne (Model 7125) injector. All chromatography was carried out at 30 °C.

3. Results and discussion

3.1. Characterization of cellulose/TiO_2 microsphere composites

Cellulose/TiO_2 microsphere composites, as abbreviated in Table 1, were prepared by a one-step phase separation method using cellulose xantate aqueous solution and sodium polyacrylate aqueous solution. Fig. 2 shows typical electron micrographs of cellulose/TiO_2 microsphere composites. All kinds of particles were perfectly spherical.

We examined the relationships among addition of diluent, pores and distribution of TiO_2 in microspheres. In the case of addition of Mw 3000,

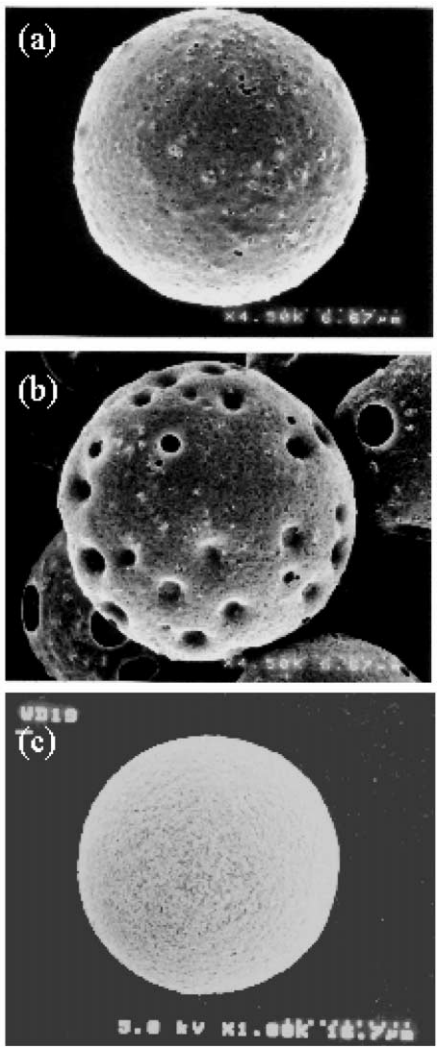

Fig. 2. Scanning electron micrographs of microsphere composites: (a) cellulose/TiO_2 microsphere composites prepared with PEG of Mw 3000; (b) cellulose/TiO_2 microsphere composites prepared with PEG of Mw 7500; (c) cellulose/TiO_2 microsphere composites without the diluent. The content of TiO_2 loaded: 20 wt.%.

polyethyleneglycol, TiO_2 particles did not appear on the surface of microspheres, as shown in Fig. 2a. In addition, in the case of adding of Mw 7500, polyethylene glycol formed macropores, as shown in Fig. 2b. In contrast, cellulose/TiO_2 microsphere composites obtained in the absence of diluent were covered with a dense arrangement of TiO_2 particle as shown in Fig. 2c. This result was also determined by surface analysis using EPMA, and is more favorable for photocatalytic decomposition. This phenomenon indicates that the distribution of TiO_2 particle is easily adjusted by adding polyethylene glycol as a diluent. Accordingly, the photocatalytic activity of the composite is easily controllable when creating the spheres.

3.2. Preparation of carbon/TiO_2 microsphere composites

Cellulose/TiO_2 microspheres prepared without diluent and covered with a dense arrangement of TiO_2 particles, were adopted as starting materials for preparing carbon/TiO_2 microsphere composites, as shown in Fig. 2c.

Fig. 3 shows scanning electron micrographs of the microsphere composites obtained in each process. All the particles obtained in each process were perfectly spherical. As the process proceeded, the microspheres were shrunk, and more TiO_2 particles appeared on the surface. This phenomenon is favorable for the photocatalytic reaction to the substrate. Table 2 shows the elemental analyses of microspheres obtained in each process and commercially activated carbon/TiO_2 composite. The carbon content increased from 33.3 to 51.5% as the processes progressed. The TiO_2 content increased from 15.6 to 41.5%, as the processes progressed, as shown in Table 2. The TiO_2 content in the microsphere composites obtained was found to be much more than that in commercially activated carbon/TiO_2 microsphere composites.

As shown in Fig. 4, X-ray diffraction revealed that the TiO_2 crystal phase in the cellulose/TiO_2 microsphere composites was anatase. In the dehydration, the X-ray diffraction pattern of cellulose disappeared. In addition, the microsphere composites carbonized in a stream of nitrogen at 600 °C were also found to have the anatase-form. Fig. 5 shows the X-ray diffraction pattern of TiO_2, commercially activated carbon/TiO_2 and carbon/TiO_2 microsphere composites. The anatase pattern of the TiO_2 in the carbon/TiO_2 microspheres was found to be much more clear than that in commercially activated carbon/TiO_2 composites. This result agrees with the elemental analysis of commercially activated carbon/TiO_2 composites. In addition, the TiO_2 content in the microspheres was easily adjusted by changing the weight ratio of the TiO_2 powder during their creation, as shown in X-ray diffraction in Fig. 6.

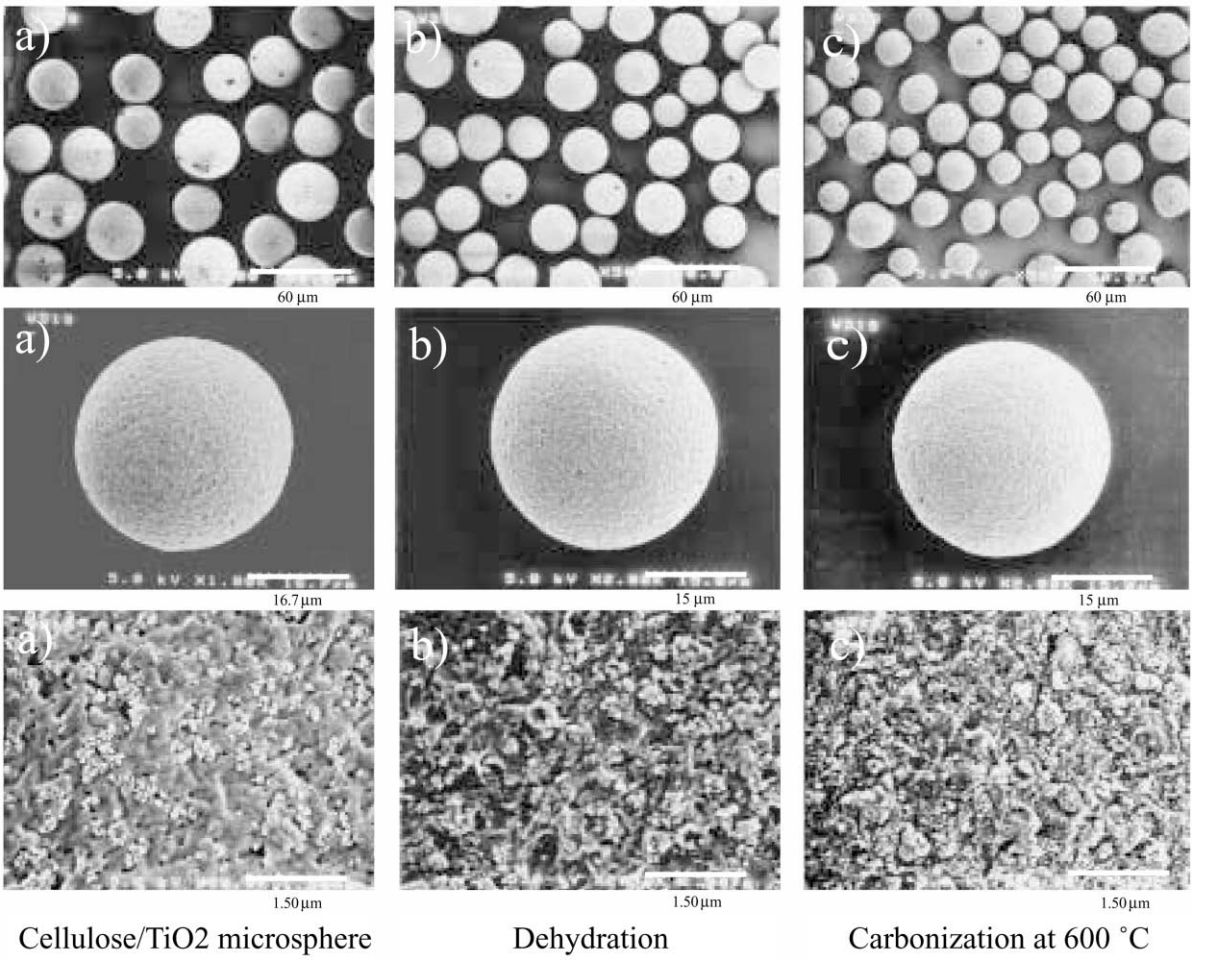

Fig. 3. Scanning electron micrographs of microsphere composites obtained in each process: (a) cellulose/TiO_2 microsphere composites freezed-drying process; (b) microsphere composites dehydrated; (c) microsphere composites carbonized.

Table 2
Microsphere composites obtained in each process

	C (%)	H (%)	TiO_2 (%)	Specific surface area (m^2/g)
Cellulose/TiO_2 microsphere composite	33.3	5.5	15.6	1.27
Cellulose TiO_2 microsphere composite removal of adsorbed H_2O	33.4	5.5	16.2	1.11
Microsphere composite dehydrated	43.4	4.2	24.0	0.91
Carbon/TiO_2 microsphere composite	51.5	1.8	41.5	0.70

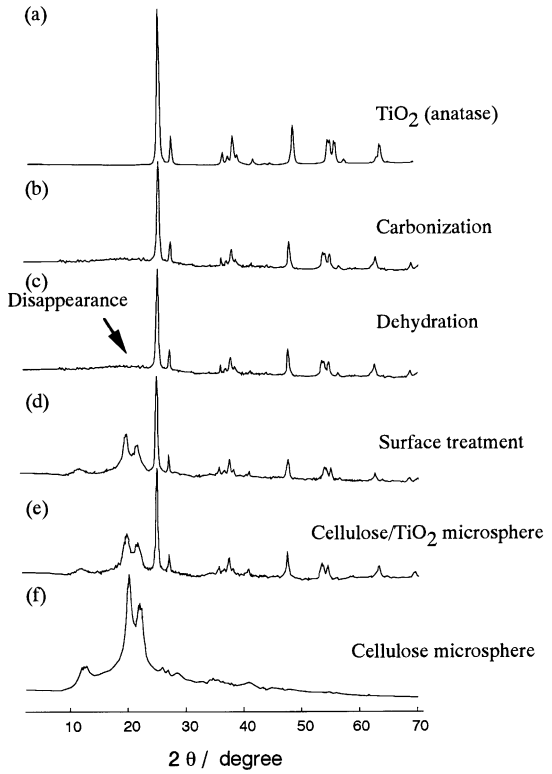

Fig. 4. X-ray diffractgrams of the beads obtained in each process, TiO_2 content, 20 wt.% for cellulose/TiO_2 microsphere composites: (a) naked TiO_2 (20 nm); (b) microsphere composites carbonized; (c) microsphere composites dehydrated; (d) microsphere composites removal process of adsorbed water; (e) cellulose/TiO_2 microsphere composites freezed-drying; (f) naked cellulose microsphere.

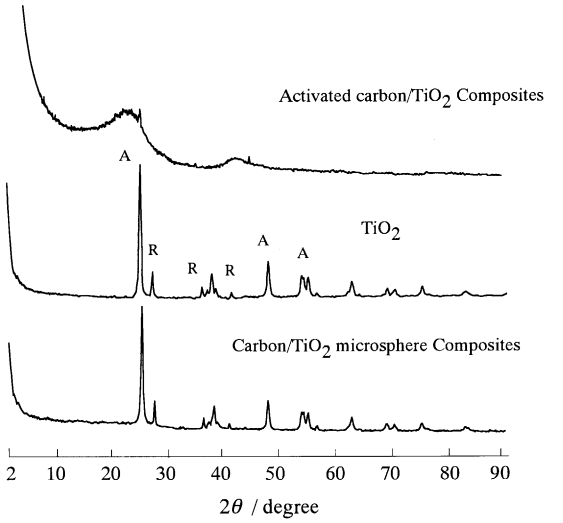

Fig. 5. X-ray diffraction patterns of activated carbon/TiO_2 composite and Carbon/TiO_2 microsphere obtained from cellulose/TiO_2. The content of TiO_2 loaded: 20 wt.%. A and R stand for anatase and rutile form, respectively.

3.3. Photocatalytic decomposition

Fig. 7 shows the time courses of the decrease in chromatogram peak area for the removal of acetaldehyde with the black lighted-off or -on carbon/TiO_2 microsphere composites and cellulose/TiO_2 microsphere composites. The increase of efficiency for removal of acetaldehyde was clearly seen with carbon/TiO_2

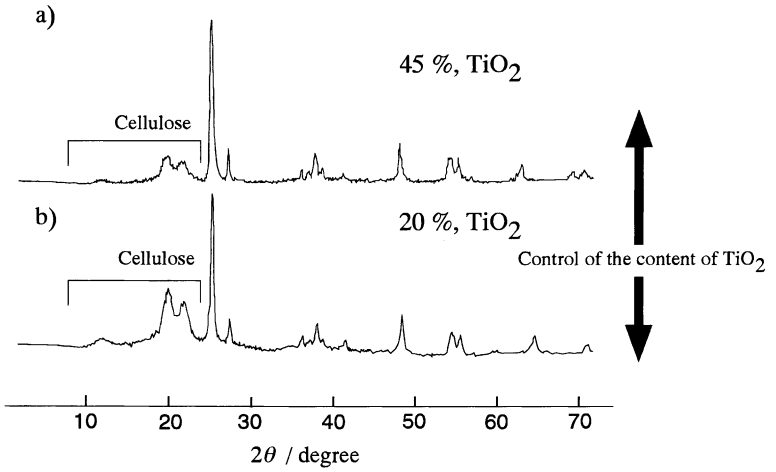

Fig. 6. X-ray diffraction patterns of cellulose/TiO_2 composite microsphere. The content of TiO_2 loaded: 45 wt.% (a); and 20 wt.% (b).

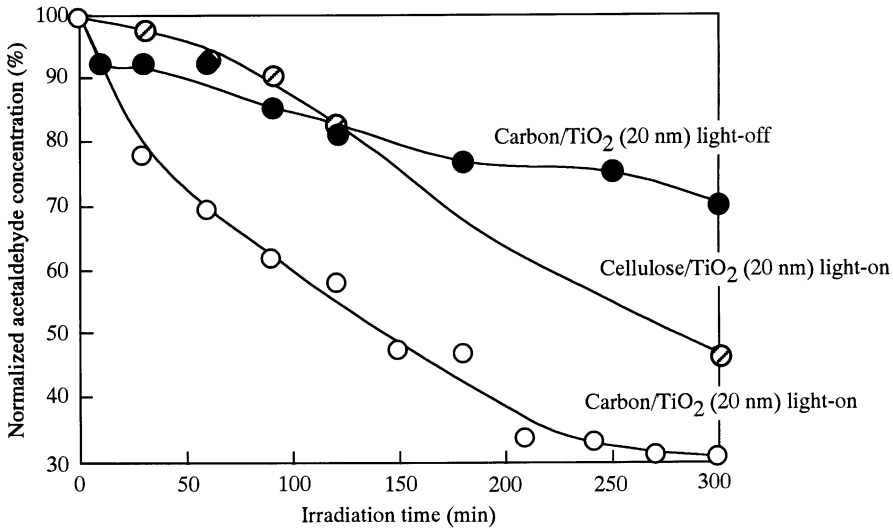

Fig. 7. Efficiency of the carbon/TiO_2 microsphere composites lighted-on (○); -off (●); and the cellulose/TiO_2 microsphere composites (⊘) for removal of acetaldehyde.

microsphere composites even under black light irradiation.

In order to investigate the effect of carbonization on the removal of acetaldehyde, the removal efficiency of the carbon/TiO_2 microsphere composites was compared with that of cellulose/TiO_2 microsphere composites adopted as starting materials. The efficiency of the carbon/TiO_2 microsphere composites for removal of acetaldehyde was much higher than that of cellulose/TiO_2 microsphere, as shown in Fig. 7. The effect of carbonization of the cellulose/TiO_2 microsphere composites was evident. The result indicates that the carbon surface was more adsorptive than cellulose surface, and so carbon support enables the

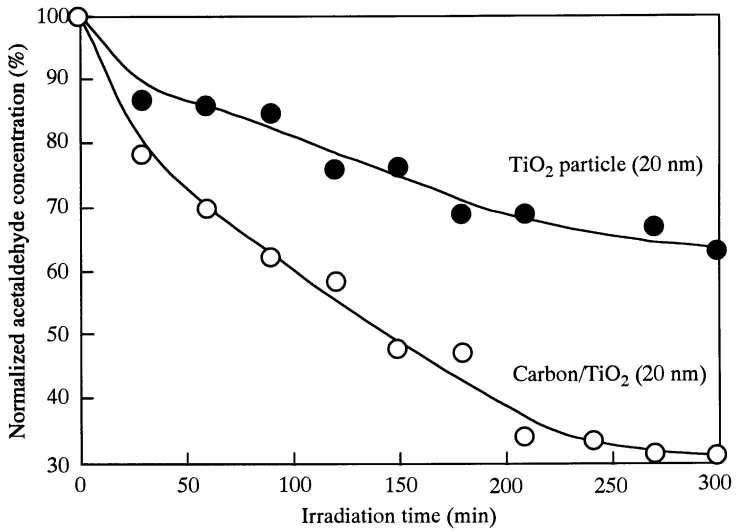

Fig. 8. Efficiency of the carbon/TiO_2 microsphere composites (○) with that of naked TiO_2 (20 nm) (●) for removal of acetaldehyde.

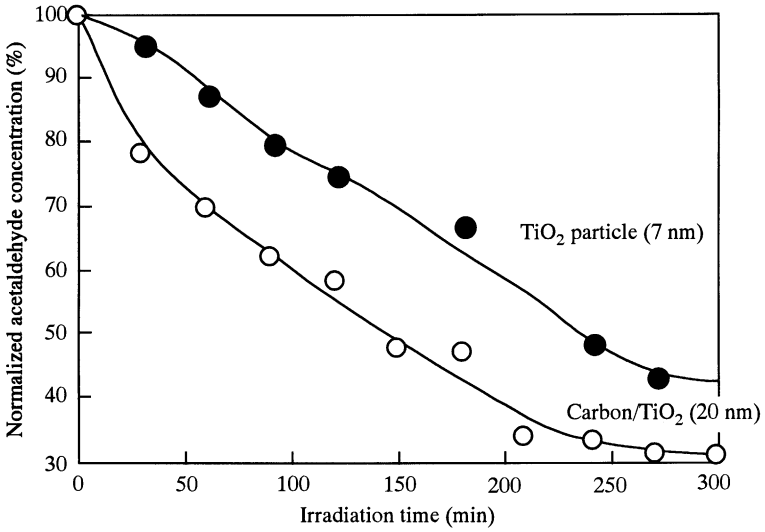

Fig. 9. Efficiency of the carbon/TiO_2 microsphere composites (○) and TiO_2 at a particle size of 7 nm (●) for removal of acetaldehyde.

organic substances to concentrate around the loaded TiO_2 photocatalysts.

Fig. 8 shows the removal efficiency of acetaldehyde in aqueous solution with naked TiO_2 (P-25) and carbon/TiO_2 microsphere composites. Illumination of the carbon/TiO_2 microsphere composites during suspension in acetaldehyde aqueous solution removed the acetaldehyde at twice the rate of naked TiO_2 (P-25).

On the other hand, the photocatalytic activity became higher with decreasing particle size [12,13]. Therefore, the photocatalytic activity of carbon/TiO_2 microsphere composites was compared using a TiO_2

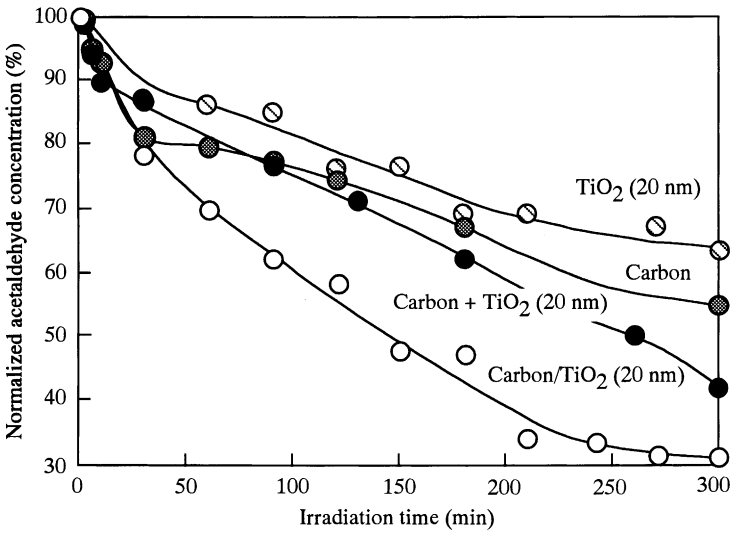

Fig. 10. Efficiency of the carbon/TiO_2 composite microsphere (○); the mixture of carbon microsphere, TiO_2(●); carbon microsphere solely (◍); and naked TiO_2 (◌) solely for removal of acetaldehyde.

particle size of 7 nm. As a result, the efficiency of the carbon/TiO_2 microsphere composites for removal of acetaldehyde was more favorable than that of TiO_2 at a particle size of 7 nm, as shown in Fig. 9.

In order to investigate the effect of hybridization of carbon and TiO_2, we compared the efficiency of removal of acetaldehyde among TiO_2 powder, carbon microspheres and carbon/TiO_2 microsphere composites, as shown in Fig. 10. The carbon showed no photocatalytic activity. Ishihara and Frutsuka reported this phenomenon in wood charcoal [14]. The removal efficiency of acetaldehyde was increased by mixing the carbon microspheres with TiO_2 powder, but the enhancement was not so great as that obtained with the carbon/TiO_2 microsphere composites. This indicates that the carbon surface was effective in concentrating acetaldehyde around the TiO_2 anchored on the composite surface [15]. The acetaldehyde seems to be supplied to the active centers of the surface of TiO_2 photocatalyst by the surface diffusion. Specifically, the specific surface area of the microspheres obtained was 0.70 m^2/g. It seemed that the small surface area of cellulose/TiO_2 microsphere composites was favorable for the photocatalytic reaction, because in the case of porous microspheres the diffusion of acetaldehyde mainly occurs at the pore sites.

4. Conclusion

The following conclusions can be drawn on the nature and characterization of the cellulose/TiO_2 microsphere composites: (1) the spherical composite is prepared by a one-step phase separation method using cellulose xantate aqueous solution and sodium polyacrylate aqueous solution; (2) the distribution of TiO_2 particles is easily adjusted by adding polyethylene glycol as a diluent. As a result, we succeeded in preparing cellulose/TiO_2 microsphere composites having surfaces covered with a dense arrangement of TiO_2 by this technique. In addition, we succeeded in carbonization of the cellulose/TiO_2 microsphere composites containing TiO_2 on the surface using the microspheres as starting materials. The following conclusions can be drawn on the nature and characterization of the carbon/TiO_2 microsphere composites (the shape of particle was a microsphere): (1) as the process of carbonization proceeded, more TiO_2 particles appeared on the surface; (2) the TiO_2 content in the microspheres was easily adjusted by changing the weight ratio of the TiO_2 powder; (3) the efficiency of the carbon/TiO_2 microsphere composites for removal of acetaldehyde was more favorable than that of naked TiO_2; and (4) the efficiency of the carbon/TiO_2 microsphere composites for removal of acetaldehyde was more favorable than that of TiO_2 at a particle size of 7 nm.

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