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Formation of TiO_2 nanotubes by thermal decomposition of poly(vinyl alcohol)-titanium alkoxide hybrid nanofibers

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Abstract Anatase type TiO_2 nanotubes were formed by calcination of poly(vinyl alcohol)-Ti alkoxide hybrid precursor nanofibers in air. The outer and inner diameters of the TiO_2 nanotubes calcined at 500 °C for 5 h were ca. 440 nm and ca. 270 nm, respectively. The specific surface area of the TiO_2 nanotubes was 38.8 m^2/g, and the existence of mesopores (average pore diameter, 14.8 nm) on the nanotube wall was indicated by the nitrogen adsorption isotherm (–196 °C). The photocatalysis of the TiO_2 nanotubes was superior to that of commercially available anatase type TiO_2 nanoparticles.

Introduction

Electrospinning is a process by which nanofibers several hundred nanometers in diameter are easily produced [1–4]. The average diameter of the fibers produced by this method is at least one or two orders of magnitude smaller than those of conventional fiber production methods like melt or solution spinning [5]. As a result, the electrospun fibers have larger specific surface area [4]. These nanofibers are well-suited to be used as chemical reaction fields [6].

Recently, much attention has been paid to the formation of both inorganic nanofibers and organic polymeric nanofibers. Inorganic nanofibers can be obtained by the thermal decomposition of organic–inorganic hybrid precursor nanofibers formed by electrospinning [7]. Li et al. formed anatase type TiO_2 nanofibers by the calcination of poly(vinyl pyrrolidone)-Ti alkoxide hybrid nanofibers in air at 500 °C [8]. The fibers would be useful material for a photocatalytic reaction, but their usage has not been investigated. Furthermore, many kinds of inorganic nanofibers (Al_2O_3, ZrO_2, $NiCo_2O_4$ and so on) have been formed from organic–inorganic hybrid precursor nanofibers [8–11].

Hanabusa et al. reported the preparation of inorganic hollow-fibers using the gelation (self-assembly with a rodlike fibrous structure) of an organogelator [12, 13]. The organogelator is a cyclohexane derivative that was specially synthesized by this research group. The outer and inner diameters of the TiO_2 hollow-fibers obtained were 150–600 nm and 50–300 nm, respectively [12]. We considered that the inorganic hollow-fibers (nanotubes) would be easily formed by using the electrospinning process without organogelators.

In this study, we formed TiO_2 hollow-nanofibers (nanotubes) by using poly(vinyl alcohol) (PVA) nanofibers, which is a commodity polymer. The precursor nanofibers of the PVA-Ti alkoxide hybrid were formed by the impregnation of Ti alkoxide into PVA nanofibers obtained by electrospinning. The photocatalytic reaction using the TiO_2 nanotubes formed was also investigated.

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Experimental

Materials

PVA (degree of polymerization: 600, saponification value: 88.1 mol%) was kindly gifted from The Nippon Synthetic Chemical Industry Co., Ltd., Japan. Titanium (Ti) tetraisopropoxide was obtained from Wako Pure Chemicals Ind., Ltd., Japan.

Formation of PVA nanofibers by electrospinning

The 14 wt% PVA aqueous solution was prepared (spinning solution) and was loaded into a plastic syringe equipped with a needle. The solution extrusion rate was 0.015 mL/min. A voltage of 25 kV was applied to the needle, and then the PVA nanofibers were collected to form non-woven mats. The collector (copper plate) was grounded, and the distance between the tip of the needle and the collector was 10 cm.

The diameter of PVA nanofiber was controlled by changing the electrospinning conditions such as the concentration of PVA solution (11–17 wt%).

Formation of PVA-Ti alkoxide hybrid precursor nanofibers and TiO_2 nanotubes

PVA-Ti alkoxide hybrid precursor nanofibers were formed as follows: The PVA nanofibers were immersed in a Ti tetraisopropoxide (10 wt%)-ethanol solution for 10 min. The treated nanofibers were washed in fresh ethanol and then dried in air. The hybrid precursor nanofibers were heated up to a given temperature in an electric furnace at 400–800 °C in air, and TiO_2 nanotubes were obtained.

Apparatus and procedure

The structure of the nanofibers and the nanotubes was observed by scanning electron microscope (SEM) (Hitachi S-2400, Japan).

X-ray diffraction (XRD) measurements were taken using a CuK_α with a Ni filter (40 kV, 30 mA) (Shimadzu XRD-6100, Japan).

The nitrogen adsorption isotherms (–196 °C) of the TiO_2 nanotubes were measured by Micromeritics TriStar 3000, USA.

The photocatalysis of the TiO_2 nanotubes was evaluated using the photocatalytic decomposition of 3,7-bis(dimethylamino)phenothiazin-5-ium chloride (methylene blue; $C_{16}H_{18}ClN_3S$) [14]. TiO_2 nanotubes formed (5 mg) were dispersed in methylene blue (1×10^{-5}mol/L) aqueous solution (50 mL). Three millilitres of test liquid was taken from this solution and fed in a quartz cell. The test solution was irradiated with white light using an extra-high pressure mercury vapor lamp (Ushio Inc., Japan), and the absorbance at 665 nm, which is the maximum absorption wavelength of methylene blue, was measured by an absorptiometer (JASCO, CT-109, Japan). The decomposition rate of methylene blue was calculated from the absorbance.

Results and Discussion

Figure 1 shows the SEM images of (a) pure PVA nanofibers formed by electrospinning, and (b) PVA-Ti alkoxide hybrid precursor nanofibers. The fiber diameter of a PVA nanofiber is ca. 200 nm, and the fiber diameter of the precursor nanofiber becomes 1.3 times larger that that of the PVA nanofiber. Both fibers have a smooth surface. White residues (TiO_2) were obtained by calcination of the hybrid precursor nanofibers at 500 °C for 5 h. The sample weight after calcination was 12.1% of the one before calcination.

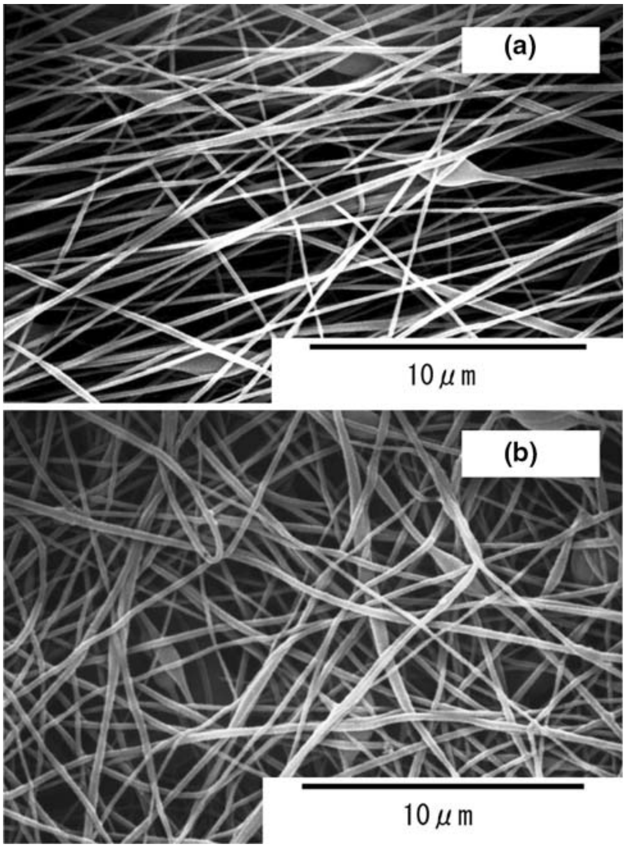

Fig. 1 SEM images of (**a**) pure PVA nanofibers and (**b**) PVA-Ti alkoxide hybrid precursor nanofibers

The residues are brittle, but maintained the shape of the precursor non-woven mat, although shrinkage occurred after calcination.

Figure 2 shows the SEM image of the residue after calcination of the precursor nanofiber at 500 °C for 5 h. As can be seen from this image, hollow TiO_2 nanofibers (TiO_2 nanotubes: outer diameter, ca. 440 nm, inner diameter, ca. 270 nm) were formed. The nanotubes obtained are seemed to have a uniform diameter as compared to the diameter range reported by Hanabusa et al. [12]. We determined that a precursor nanofiber with a skin-core structure would be obtained by our method; the skin layer is a PVA-Ti alkoxide hybrid, and the core is pure PVA. Ti alkoxide will penetrate into the PVA matrix when the PVA nanofibers are immersed in Ti alkoxide-ethanol solution, and a PVA-Ti alkoxide hybrid layer will be formed. The interaction between the PVA and Ti alkoxide cannot be identified, but the hybrid would be formed by a coordination bond between the titanium and oxygen of the hydroxyl group on the PVA molecules [15]. The structure of the TiO_2 nanotubes obtained would be reflected in the skin-core structure of the precursor nanofibers.

The diameter of the nanotube can be controlled by changing the diameter of the pure PVA nanofiber. However, nanotubes were not obtained when the outer diameter was ca. 200 nm (Fig. 3(a), formed of non-hollow nanofibers) or ca. 700 nm (Fig. 3(b), breaking of TiO_2 tube wall). The range of the outer diameter which can be formed in this study is 300–600 nm.

Figure 4 shows the XRD curves of the residues (TiO_2) obtained by calcination of the precursor nanofibers at 400–800 °C for 5 h. Anatase type TiO_2 is formed at 400–600 °C, and the peak intensity increases with an increase in the calcination time. Rutile type (rutile-anatase mixed) TiO_2 is formed above 600 °C. It is well-known that anatase is superior to rutile for photocatalysis. Thus, a calcination temperature of 500–600 °C would be a good condition when using the TiO_2 nanotubes as a photocatalyst.

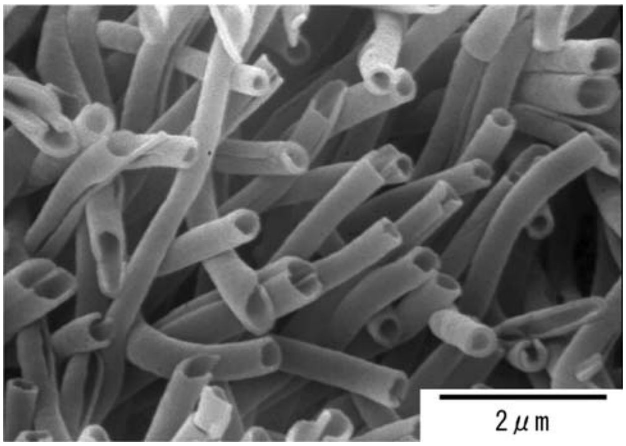

Fig. 2 SEM image of TiO_2 nanotubes formed by calcination of PVA-Ti alkoxide hybrid nanofibers at 500 °C for 5 h in air

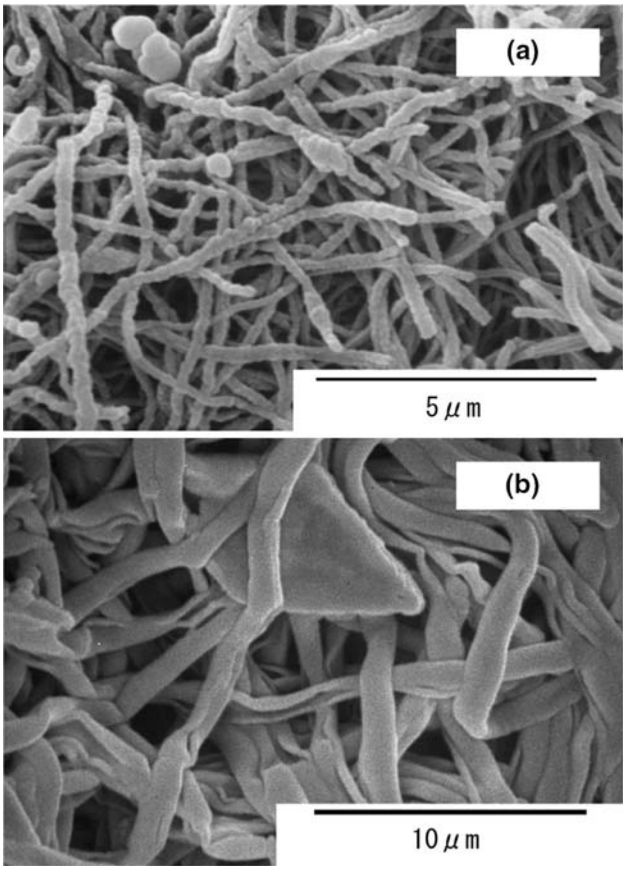

Fig. 3 SEM images of (**a**) non-hollow TiO_2 nanofibers and (**b**) wall-broken TiO_2 nanotubes

Figure 5 shows the nitrogen adsorption isothermes (–196 °C) of the TiO_2 nanotubes (calcination temperature range: 400–700 °C). The adsorption amount of the TiO_2 nanotubes decreases with an increase of the calcination temperature. This is due to the sintering of TiO_2. The specific surface areas of the TiO_2 nanotubes were obtained from Fig. 5 using the B.E.T. equation. The areas are 75.9 m^2/g (calcination at 400 °C), 38.8 m^2/g (500 °C), 17.4 m^2/g (600 °C) and 6.4 m^2/g (700 °C) (the area of pure PVA nanofiber was 3.8 m^2/g). The average pore diameters (d_p), which were assumed as a cylindrical pore shape, were calculated from the specific surface area (S) and pore volume (V: determined from the nitrogen adsorption amount at $P/P_0 = 0.98$) for each TiO_2 nanotube: $d_p = 4$ V/S. The d_p of the TiO_2 nanotubes were 8.3 nm (400 °C),

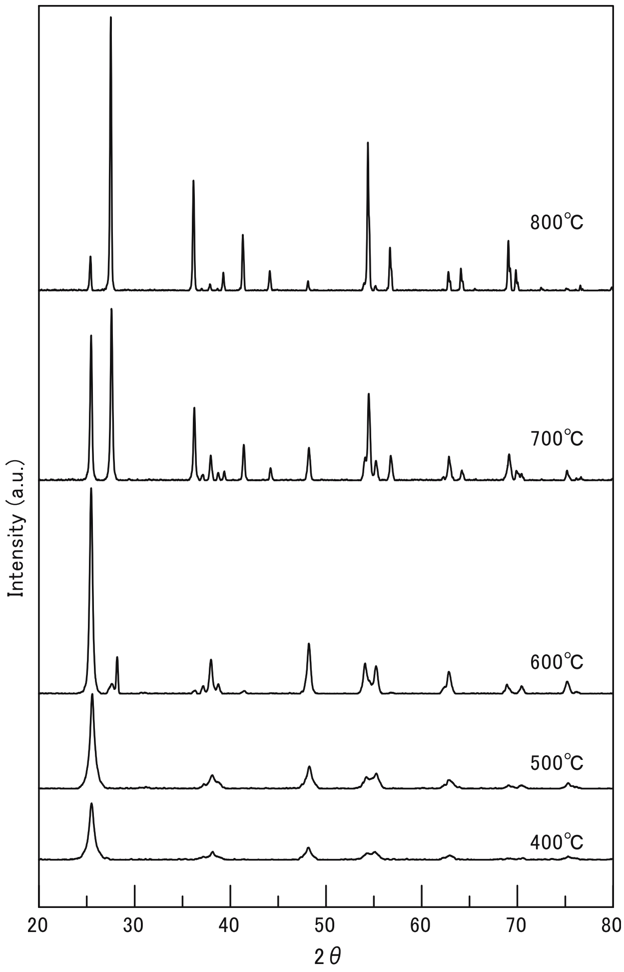

Fig. 4 XRD of TiO_2 calcined at various temperatures in air

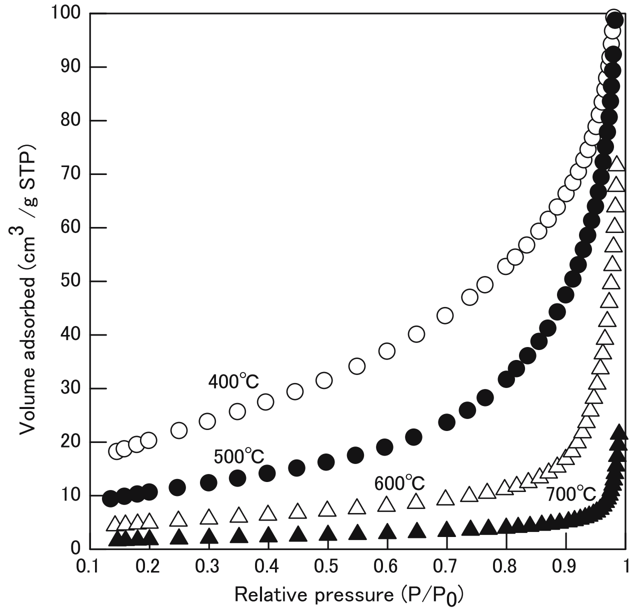

Fig. 5 Nitrogen adsorption isotherms (–196 °C) of TiO_2 nanotubes calcined at various temperatures

14.8 nm (500 °C) and 21.4 nm (600 °C). These pore sizes are not reflected the hollow size of the TiO_2 nanotubes, because the hollow size is several hundred nanometers (see Fig. 2). Therefore, it is likely that the TiO_2 nanotubes have mesopores on their nanotube wall. The mesopores would be through-holes formed by thermal decomposition of PVA in the precursor hybrid nanofibers. By the presence of the mesopores, the specific surface area of the TiO_2 nanotubes becomes larger, and the photocatalytic reaction using the TiO_2 nanotubes would occur effectively. The TiO_2 nanotube calcined at 700 °C had a non-porous wall due to the sintering.

The photocatalysis of the TiO_2 nanotubes and commercially available anatase type TiO_2 nanoparticles (Ishihara Sangyo Kaisha, LTD.: ST-21, particle size: 20 nm, specific surface area: ca. 50 m^2/g) was investigated. Figure 6 shows the relationship between the decomposition rate of methylene blue and the irradiation time of white light for each TiO_2. The photocatalysis of the anatase type TiO_2 nanotube (calcination at 500 °C and 600 °C) is higher than that of ST-21, and the nanotube (calcination at 600 °C) shows the highest photocatalysis in this experiment. Also, the photocatalysis of the rutile-anatase mixed TiO_2 nanotube (calcination at 700 °C) is equivalent to that of ST-21. The specific surface area of ST-21 is higher than that of TiO_2 nanotubes, but the TiO_2

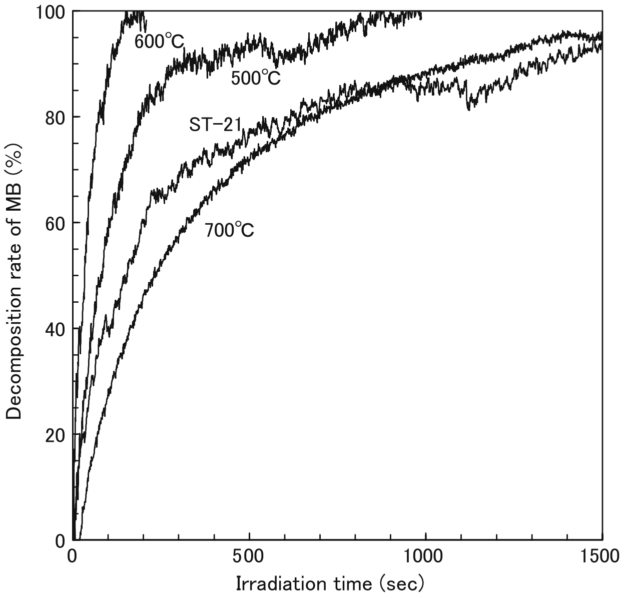

Fig. 6 Effect of irradiation time of white light upon the decomposition rate of methylene blue by the photocatalysis of TiO_2 nanotubes calcined at various temperatures and commercially available TiO_2 nanoparticles (ST-21)

nanotubes excel in photocatalysis. At the present stage the reason is uncertain, but the structure of the nanotube with mesopores on its tube wall might contribute to the efficient photocatalysis of TiO_2.

Conclusions

PVA-Ti alkoxide hybrid precursor nanofibers were formed by the immersion of pure PVA nanofibers in Ti tetraisopropoxide-ethanol solution. TiO_2 nanotubes were easily formed by calcination of the hybrid precursor nanofibers. The nanotubes obtained had a high specific surface area and the existence of mesopores on the nanotube wall was indicated by the nitrogen adsorption isotherms. The photocatalysis of the TiO_2 nanotubes was superior to that of commercially available anatase type TiO_2 nanoparticles.

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