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Synthesis of effective titania nanotubes for wastewater purification

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ABSTRACT

In order to synthesize a self-organized, TiO_2 nanotubular layer for wastewater purification, anodizations were performed at constant applied potential in hydrofluoric acid and the anodic TiO_2 layer was heat treated. The anodic nanotube arrays were also influenced by the applied anodic potentials and HF concentrations. The anodic TiO_2 nanotubular structured film with various morphologies and crystal structures can be synthesized by proper electrochemical anodization and additional annealing treatment. The photocatalytic efficiencies were maximized for the anatase-type, TiO_2 nanotubular layer which was prepared by annealing at 550 °C.

1. Introduction

Recently many studies have investigated titanium dioxides (TiO_2) due to their varieties of functional properties. Especially, TiO_2 nanotube structure has attracted considerable interest because of its large surface area and potential technological applications such as biomaterial [1], gas sensor, and photocatalysis [2,3]. In general, the self-organized nanotubular layer [4–6] can be achieved at anodic potential range lower than 40 V, but to maximize the wide applications for the titania nanotubes with various functional properties, the characteristics of TiO_2 nanotubes, including microstructure, crystallinity, and film thickness, need to be investigated. However, there are few reports of these synthesis parameters. In this study, therefore, the TiO_2 nanotubes with functional properties were synthesized by anodic oxidation in hydrofluoric (HF) solution. To investigate the fabrication parameters of the titania nanotubes, we examined the effects of applied anodic potential and electrolyte concentration on the formation of self-organized anodic TiO_2 nanotubes. Because the anodic TiO_2 nanotube prepared in HF electrolyte has not only a high chemical stability but also the advantage of a high specific surface area, it can be applied to photocatalysts for the degradation of organic pollutants in aqueous media. Among photocatalysts, the photocatalytic efficiency of the anatase-type TiO_2 crystal structure is known to be more effective than that of other crystal structures. However, the anodic nanotubular film consists of an amorphous TiO_2 structure. To transform the crystal structure, the anodic titania films were annealed at 450, 550, and 650 °C for 1 h, and the photocatalytic efficiency was investigated.

2. Experimental

The substrate used was a commercial grade, pure titanium plate (99.6 wt.%). After the titanium specimens were pretreated and degreased in *n*-hexane, the anodic titania nanotubes were synthesized by anodization in HF solutions at a constant potential. The crystalline structure on the anodic TiO_2 layer was characterized by X-ray diffraction (XRD; Philips, Model PW1710). The microstructures on the anodic TiO_2 nanotubes were observed using a field emission scanning electron microscope (FE-SEM, Philips XL30 ESEM-FEG). To investigate the light absorption properties of titania films, analysis of reflectance absorption spectra was performed using a UV–vis spectrophotometer (Cary 500 Scan UV–vis–NIR spectrophotometer) with a wavelength range of 250–550 nm.

The dye and dichloroacetic acid (DCA) decomposition rates of the anodic TiO_2 film were evaluated using a Pyrex glass reactor with a diameter of 70 mm and a height of 20 mm at 25 °C. The apparent geometrical irradiation area of the TiO_2 specimens as the

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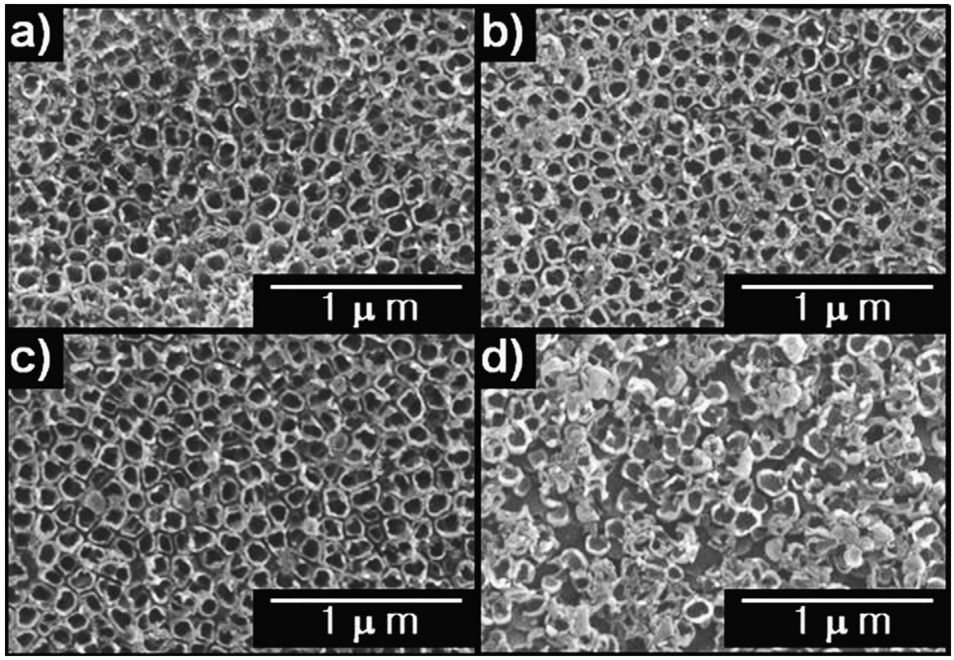

Fig. 1. Morphologies of self-organized nanotube arrays on anodic titania. The anodic TiO_2 nanotube films formed at 20 V in 0.5 wt.% (a), 1.0 wt.% (b), 2.0 wt.% (c), and 3.0 wt.% (d) HF solution.

photocatalyst was 10.5 cm^2. For the photocatalytic experiment, 83 μM aniline blue solution (Fulka, pH 4) and 0.48 mM DCA (Aldrich, 99%, pH 5.7) solutions were prepared. All of the experiments for photocatalytic reaction were performed with 30 mL solution and using a 100 W Hg lamp as the light source. UV–vis spectroscopy (Unicam 8700) was performed to determine the decomposition rate of the dye at the absorption band of 600 nm. Dichloroacetic acid decomposition rate was carried out using a Total Organic Carbon (TOC) analyser (Shimadzu 5000) with a combustion/non-dispersive infrared gas analysis method.

3. Results and discussion

3.1. Effects of electrolytes

In order to investigate the effect of HF solution concentration on the self-organized nanotubular structure in anodic titania film, the

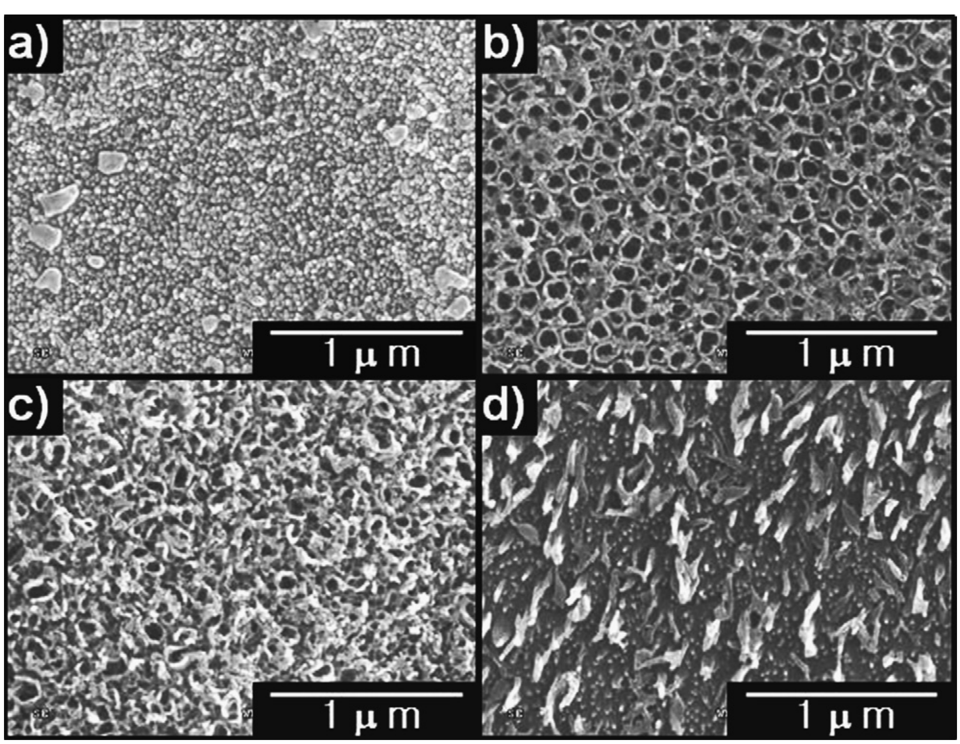

Fig. 2. Nanotubular arrays in anodic titania prepared by anodization in 2 wt.% HF solution for 40 min at 15 V (a), 20 V (b), 25 V (c), and 40 V (d).