Synthesis Optimization and Characterization of Visible-light Responsive Ce-doped Titanate Nanotubes for Enhanced Degradation of Polluting Dyes in Aqueous Environment

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For the decomposition organic substrates in the reaction container, we developed Ce-doped titanate nanotubes as visible light responsive photo catalyst. Anatase titania and titanate nanotubes were prepared using the sol-gel method and hydrothermal method. The photoactivity of Ce-doped titanate nanotubes under visible light were dramatically improved than anatase titania and titanate nanotubes. All titania and titanate nanotubes were characterized using X-ray diffraction, field emission scanning electron microscopy, inductively coupled plasma-atomic emission spectroscopy and UV-Vis absorption spectroscopy. Their’s photocatalytic activities were investigated by the degradation rate of methylene blue solution under UV and visible light condition. The crystalinity of the titanate nanotubes were increased by Ce-doping compared with that of pure titania nanotube. In addition, the UV-Vis absorption ranges of Ce-doped anatase titania and Ce-doped titania nanotube were red shifted by Ce-doping. These morphology changes to nanotubes with Ce-doping will be very useful for practical application for decomposing color dyes included amino group in the wasted water.

Keywords: Ce doping, photocatalyst, TiO₂, titanate nanotubes, visible light photoactivity

INTRODUCTION

After the first report of the photocatalytic activity of titania (TiO₂) by Fujishima and Honda (1972), plenty of researches have been conducted on TiO₂. TiO₂ is a particularly attractive photocatalyst, because the functionality, safety, stability, resources and cost of TiO₂ are more superior rather than other photocatalysts such as ZnO, ZrO and WO₃. Recently, TiO₂ has been commonly used in self-cleaning materials that can decompose organics, NOₓ, and SOₓ, and as the substrate of dye-sensitized solar cells (DSC) (O’Regan and Grätzel, 1991; Ibusuki and Takeuchi, 1998) discovered a simple synthetic method for the preparation of titanate nanotubes. After this report, a lot of researches have been conducted on TiO₂ (1998) by mixing and calcinations. In another application study of adsorption/decomposition, Nazir et al. (2003) reported NH₃ gas decomposition using TiO₂ on the activated carbon. Although colored effluents are frequently lower level pollutants than many colorless effluents, they are also considered as an indicator of pollution, especially the decomposition and elimination of dyes in textile wastewater has been studied (Bestania et al., 2008).

When TiO₂ is used as decomposition organic substrates in the reaction container, high photoactivity in visible light irradiation is quite important in terms of cost. Because typically TiO₂ works as a photocatalyst only under UV light irradiation, Quarts glass required for incident path/windows material. In addition, UV light slightly needs much cost than visible light and also causes problems such as sunburn, stain, and skin cancer of operation stuff. To improve these problems, the development of photocatalyst responsive to visible light is useful.

Visible light responsive TiO₂ has been prepared by typical two methods; surface modification and ion doping (ex. Fe, Cu, other transition metal, rare earth ions, and non-metal ions such as S and/or N) (Ohno, 2005; Sathish et al., 2005; Zhou et al., 2005; Xiao et al., 2007; Xiaoyuan et al., 2008; Xue et al., 2011) by mixing and calcinations. In these reports, photoactivity were reduced by transition metal ion doping and non-metal doping titania had a disadvantage that it cannot be used repeatedly in the water.

Titania nanotube is expected to be a high performance photocatalyst, because titania nanotube has a large surface area, high adsorption ability with ion exchange capacity and superior charge transport property (Bevykin and Walsh, 2009; Hernández-Alonso et al., 2011). Kasuga et al. (1998) discovered a simple synthetic method for the preparation of titanate nanotubes. After this report, a lot of researchers have been reporting for their structures, physical properties, crystal growth mechanism, photoactivity and etc. (Hu et al., 2011; Xue et al., 2011). Titanate nanotubes adsorb and decompose positive ion organic species, espe-
cially color dye including the azo- and amino-group (Babitha et al., 2014).

We have attempted to synthesize visible light responsive Ce-doped titanate nanotubes for colorless of water. The synthesized samples were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and UV-Vis absorption spectroscopy to understand the morphology, structure and spectroscopic properties of TiO$_2$ nanotube. We select the methylene blue (MB) as color dye including a amino-group. The photocatalytic activities of samples were investigated by the degradation of MB solution under UV and visible light irradiations.

**EXPERIMENTAL SECTION**

**Synthesis of Ce-doped titania nanotube**

The so-gel method was used for the following synthetic procedure. Since we have reported that the particle size of anatase TiO$_2$ could be controlled in the previous work (Yoshizuka et al., 2009), we apply this procedure for preparing Ce-doped anatase TiO$_2$ and Ce-doped titanate nanotube. Firstly, trichloride cerium was added to tetrachloride titanium solution to prepare the composition with Ce : Ti = 100 : 1.3 (wt%). Titanium hydroxide was obtained by mixing with 1wt% NH$_3$ solution and tetrachloride titanium solution. After washing with deionized water, titanium hydroxide was oxidized by hydrogen peroxide, to produce amorphous TiO$_2$. Ce-doped anatase TiO$_2$ gel was obtained by the hydrothermal method (120°C, 12 h). The Ce-doped anatase TiO$_2$ gel was then dried to obtain the powdery anatase TiO$_2$.

The powdery Ce-doped anatase TiO$_2$ was added to 10 mol L$^{-1}$ NaOH solution and heated at 110°C for 24 h by hydrothermal treatment. Hydrochloric acid (0.1 and 1 mol L$^{-1}$) was then added for neutralization, and the product was washed with deionized water and dried. The Ce-doped titanate nanotube obtained was colored creamy white.

**Characterization of samples**

Characterization of samples was carried out using FE-SEM (Hitachi S-5200, Japan), XRD (Rigaku Ultima$^+$), ICP-AES (Perkin Elmer Optima 4300DV, USA) and UV-Vis absorption spectroscopy (Jasco UV-660, Japan). The degradation rate of MB in the aqueous solution was measured to obtain the photocatalytic activity. As a pretreatment, 50 mL of MB solution (100 μmol L$^{-1}$) was mixed with 0.01 g of sample and shaken for 2 d to ensure the complete adsorption of MB on the samples. After adsorption, the samples were set into 35 mL MB solution (10 μmol L$^{-1}$) and irradiated with UV and visible lights using a solar simulator (Yamashita Denso YSS-50, 100 mW cm$^{-2}$, Japan) under constant stirring. Absorption intensity of 644 nm by UV-VIS were measured in 5–10 min interval.

**RESULTS AND DISCUSSION**

The particle size of pure anatase TiO$_2$ was 15–20 nm and that of the Ce-doped anatase TiO$_2$ was smaller at 10–15 nm (Fig. 1). The diameters of the pure titanate and Ce-doped titanate nanotubes were approximately 10–20 nm, and the length was typically < 1 μm. No differences between pure and Ce-doped TiO$_2$ nanotubes were indicated by FE-SEM observation (Fig. 2).

The X-ray patterns of Ce-doped anatase TiO$_2$ and pure anatase TiO$_2$ are shown in Fig. 3(a) and (b), and those of Ce-doped anatase titanate nanotube and pure anatase titanate nanotube are also shown in Fig. 3(c) and (d). These peaks of nanotubes are indicated H:TiO$_2$. No peaks of Ce-oxide and Ce-chloride (ex. CeO or CeCl$_3$) were observed for Ce-doped anatase TiO$_2$ and Ce-doped titania nanotube. The crystallinities of the TiO$_2$ nanotubes were...
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increased by Ce-doping, because the H2-Ti3-O7 peak was sharper than that of the pure titanate nanotubes.

The Ce concentrations in Ce-doped anatase TiO2 and Ce-doped titanate nanotubes were measured by ICP-AES as listed in Table 1. These results indicate that the amount of Ce is reduced by approximately 1/3 of anatase TiO2 during the synthesis process. Regardless of the initial Ce concentration, they are almost constant (≈0.4%).

Figure 4 shows the UV-VIS absorbance spectrum of the samples. The absorption edge of Ce-doped anatase TiO2 was shifted to the red (450 nm). In contrast, the absorption edge of Ce-doped titanate nanotube was shorter than one of Ce-doped anatase TiO2, although the ability to absorb visible light (edge wavelength value was around 420 nm) still remained.

The photocatalytic activities of the samples are shown in Fig. 5(a) and (b) and Table 2. Since the degradation of MB was a first order reaction, the rate of MB degradation was calculated using the following equation:

$$L_o \left( \frac{C_t}{C_0} \right) = -k_t$$

where \(C_t\) and \(C_0\) are the MB concentrations in the aqueous solution at time \(t\) and at the start time, respectively, \(k_t\) is the first order reaction rate constant (\(k_t\) is intended photocatalytic activity). A UV cut filter (cut off point=380 nm, cut off rate ≥99%) was used for the visible light conditions. Pure titanate nanotube exhibited the highest photocatalytic activity under UV light irradiation, and the Ce-doped titanate nanotube showed the highest photocatalytic activity under visible light. The results are consistent with the absorbance spectra. The photocatalytic activity of Ce-doped titanate nanotube was over 100 times higher than that of pure anatase TiO2 under visible light irradiation.

### CONCLUSIONS

We synthesized pure anatase and Ce-doped anatase using sol-gel method and hydrothermal method. We also synthesized pure titanate and Ce-doped titanate nanotubes.

### Table 1  Ce dopant concentration by ICP measurement.

| Sample                         | Amount of Ce (wt%) |
|--------------------------------|--------------------|
| Ce-doped anatase TiO2          | 1.30               |
| Ce-doped TiO2 nanotube         | 0.40               |
| Ce-doped TiO2, nanotube        | 0.44               |

### Table 2  Photocatalytic activity obtained by the degradation of MB solution (\(k \times 10^{-3}\)).

| Samples                        | \(k\) (under UV)/min | \(k\) (under Vis)/min |
|--------------------------------|----------------------|-----------------------|
| Pure anatase TiO2              | 2.571                | 0.07004               |
| Ce-doped TiO2                  | 0.9607               | 0.4830                |
| Pure TiO2 nanotube             | 5.850                | 4.749                 |
| Ce-doped TiO2 nanotube         | 5.678                | 8.364                 |
from pure anatase titania and Ce-doped anatase titania. The crystallinity of the titanate nanotubes structures was increased by Ce-doping. Moreover, the absorption ranges of Ce-doped anatase TiO₂ and Ce-doped titanate nanotubes were shifted to visible light range. The Ce-doped nanotubes exhibited best photocatalytic activity under visible light conditions; Ce-doped titanate nanotube exhibited more than twice higher photocatalytic activity under UV light irradiation and also more than 100 times higher under visible light irradiation compared with that of pure anatase TiO₂. These morphology changes to nanotubes with Ce doping will be very useful for practical application for decomposing color dyes included amino group in the wasted water.

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