AAO-template assisted synthesis and size control of one-dimensional TiO_2 nanomaterials

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Anodic aluminum oxide (AAO)-template method is a synthesis process that AAO film with uniform pores is used as a template for 1-D nanostructure. In this study, we have synthesized well-defined TiO_2 nanorods or nanowires using AAO-template method. As for the first method, AAO template was immersed for 1 min in the Ti precursor solution with slightly decompressed atmosphere (Immersion setting, IS). As for the second method, AAO template was put on the filtering flask as a cover plate. Precursor solution was dropped on the AAO template for 1 min with vacuuming from the bottom part of AAO template (Vacuum and drop setting, VDS). With the calcination and HCl treatment to remove AAO, polycrystalline TiO_2 anatase nanorods and nanowires were successfully fabricated, just by changing the sample setting, *viz*., IS and VDS, respectively.

Key-words : TiO_2, Nanorod, Nanowire, Anodic aluminum oxide (AAO), Tetraisopropyl orthotitanate

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1. Introduction

Titanium dioxide, TiO_2, is widely used for cosmetics, electric devices, photocatalysts, dye-sensitized solar cells, and so on.[1)–5)] Recently, one-dimensional (1-D) TiO_2 nanomaterials have been extensively studied to enhance the functionality of TiO_2,[6)–14)] due to their large surface area and high crystallinity. 1-D TiO_2 nanomaterials are promising not only for photocatalysts and dye-sensitized solar cells but also lithium ion batteries and gas sensors. Depending on the various applications of TiO_2, morphology (e.g., length, thickness, diameter) and crystallinity are desired to be optimized. A variety of methods have been reported to synthesize 1-D TiO_2 nanomaterials. Among them, three methods are typically used, *viz*., (1) hydrothermal method, (2) anodic oxidation method and (3) AAO-template method.

(1) Hydrothermal method is a synthesis process that precursor materials are typically dissolved in alkaline aqueous solution and heated at 100–150°C for several days.[6)–10)] This method is relatively mass-productive. However, the size control, in particular for the length of 1-D structure, is not so precise. (2) Anodic oxidation method is a synthesis process that TiO_2 membrane with a large number of uniform pores is produced by the surface electric oxidation of Ti electrode.[11)–14)] TiO_2 membranes with well-ordered pores are obtained from this method, however, it is difficult to separate each nanotube from membranes. In addition, applicability of anodic oxidation method is limited for a certain metals. (3) The anodic aluminum oxide (AAO)-template method is a synthesis process that AAO film with uniform pores is used as a template for 1-D nanostructure.[15)–20)] Typically, chemical solution processes are combined to this process to obtain uniform 1-D nanomaterials. By using this method, well-controlled separate 1-D TiO_2 nanomaterials can be obtained.

In this study, we have synthesized well-defined TiO_2 nanorods or nanowires using AAO-template method. Just by changing the sample setting, *viz*., (a) immersion setting (IS) and (b) vacuum and drop setting (VDS), nanorods and nanowires were selectively fabricated, respectively.

2. Experimental

2.1 Starting materials

$C_{12}H_{28}O_4Ti$ (tetraisopropyl orthotitanate, TTIP), $(CH_3)_2CHOH$ (isopropanol, i-PrOH) and $C_5H_8O_2$ (acetylacetone: ACA) were used as Ti-precursor, solvent and chelating agent, respectively.[11),19)] The addition of ACA is effective to slow down the hydrolysis reaction of TTIP. The compositions of regents were TTIP: ACA = 1:1 (in molar ratio), and TTIP: (ACA + i-PrOH) = 1:4 (in volume ratio). TiO_2-precursor solution was prepared as follows. ACA was dropwisely added to TTIP, resulting into a yellowish solution. And then, i-PrOH was dropped to the TTIP-ACA solution, giving light-yellowish transparent solution.

2.2 Sample preparation

Anodic aluminum oxide membranes (AAO, Anodisc13, Whatman) are used as the template for 1-D TiO_2 nanomaterials. The macroscopic diameter and thickness of AAO were 13 mm and 60 µm and the through-hole diameter was 200 nm. We used two settings to insert the precursor solution into pores of AAO template. As for the first method, AAO template was immersed for 1 min in the precursor solution with slightly decompressed atmosphere (Immersion setting, IS) [**Fig. 1**(a)]. As for the second method, AAO template was put on the filtering flask as a cover plate [Fig. 1(b)]. Precursor solution was dropped on the AAO template for 1 min with vacuuming from the bottom part of AAO template (Vacuum and drop setting, VDS). Subsequent experimental procedures of IS and VDS were same. After inserting precursor solution, AAO membranes were left in the air for

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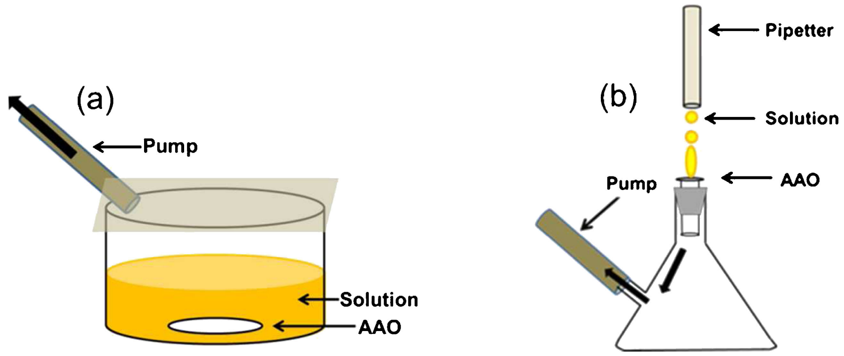

Fig. 1. Schematic illustrations of AAO-template method: (a) immersion setting (IS), and (b) vacuum and drop setting (VDS).

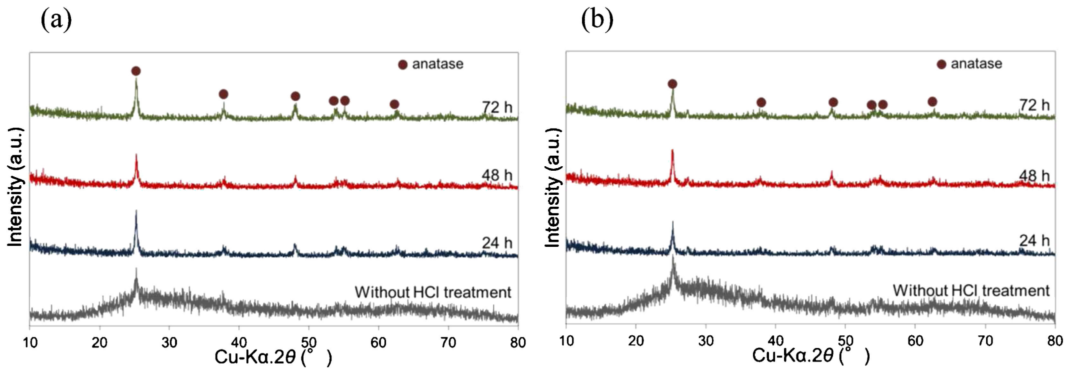

Fig. 2. XRD patterns of the samples without HCl treatment and with HCl treatment at 40°C for 24, 48, 72 h: (a) immersion setting (IS), and (b) vacuum and drop setting (VDS).

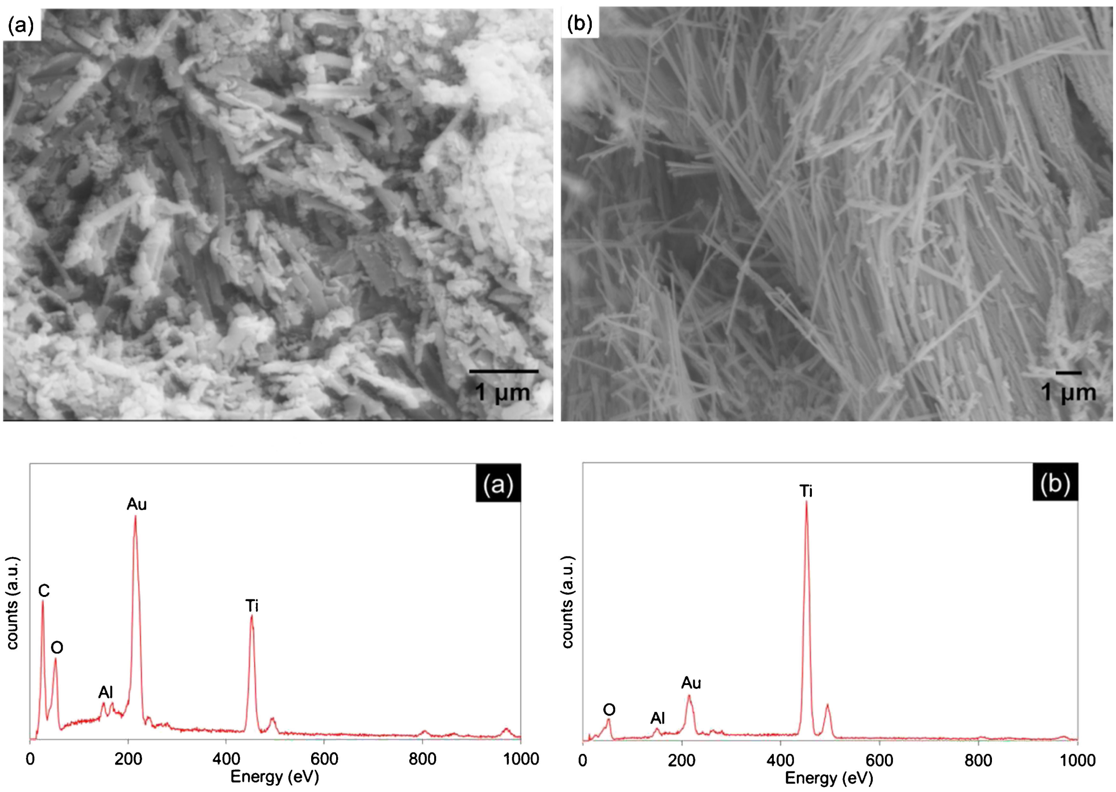

Fig. 3. SEM images and EDS spectra of the samples prepared by (a) immersion setting (nanorods) and (b) vacuum and drop setting (nanowires), respectively. EDS spectra confirmed that AAO was successfully removed from the samples. C and Au peaks are from carbon tape and surface coating.

30 min to let precursor solution hydrolyze. By the hydrolyzation, AAO membranes changed into whitish due to the deposition of TiO_2. Then, the samples were calcined at 700°C for 1 h in air. After calcination, samples were treated by 1 M HCl to remove AAO template from samples.[18),20)] The samples after calcination were put in a centrifuge tube filled with 1 M HCl, and they were mildly heat-treated at 40°C for 24 h, 48 h or 72 h. After the HCl treatment, samples were separated into solid phase (TiO_2) and liquid phase by centrifugation (10000 rpm).

2.3 Characterization

Crystal structure of samples was identified by X-ray diffraction (XRD; 40 kV, 40 mA, Rigaku, Mutiflex, Japan). The microstructure of 1-D nanomaterials was observed by scanning electron microscopy (SEM; JSM-6500F, JEOL, Japan). Au was coated for SEM analysis to avoid charging. The chemical composition was qualitatively analyzed by energy-dispersive X-ray spectroscopy (EDS; EDAX, EDAX Inc., U.S.A.). The microstructure of 1-D nanomaterials was also studied by transmission electron microscopy (TEM; JEM-2100, JEOL, Japan).

3. Result and discussion

3.1 XRD analysis

Figure 2 demonstrates XRD patterns of the samples synthesized by AAO-template method using (a) immersion setting (IS) and (b) vacuum and drop setting (VDS): sample without HCl treatment, and samples with HCl treatment for 24, 48 and 72 h. As for the IS samples [Fig. 2(a)], without HCl treatment, broad peaks of the amorphous templates (AAO) as well as weak peaks of anatase TiO_2 were observed. With 24–72 h HCl treatment, the broad peaks of AAO disappeared, and the peaks of anatase TiO_2 were only observed. These results indicated that AAO templates were successfully removed by the HCl treatment ≥24 h. The samples by VDS setting exhibited similar XRD patterns [Fig. 2(b)].

3.2 Microstructure

Figure 3 shows SEM micrographs and EDS spectra of the samples synthesized by AAO-template method using (a) immersion setting (IS) and (b) vacuum and drop setting (VDS). In Fig. 3(a), plenty of TiO_2 nanorods with the length of 500 nm–

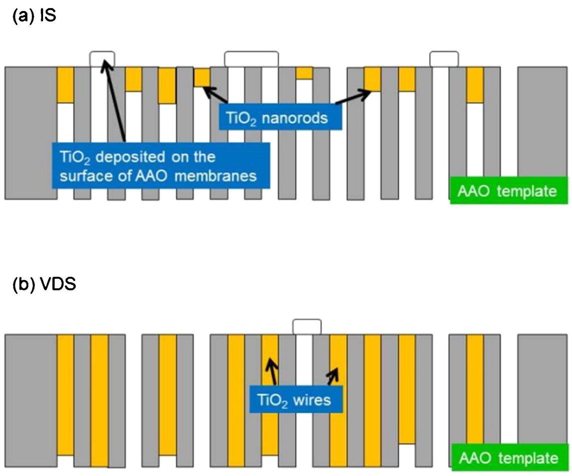

Fig. 4. Schematic illustrations of the sample preparation: (a) immersion setting (nanorods) and (b) vacuum and drop setting (nanowires), respectively. Some TiO_2 particles deposited on the surface.

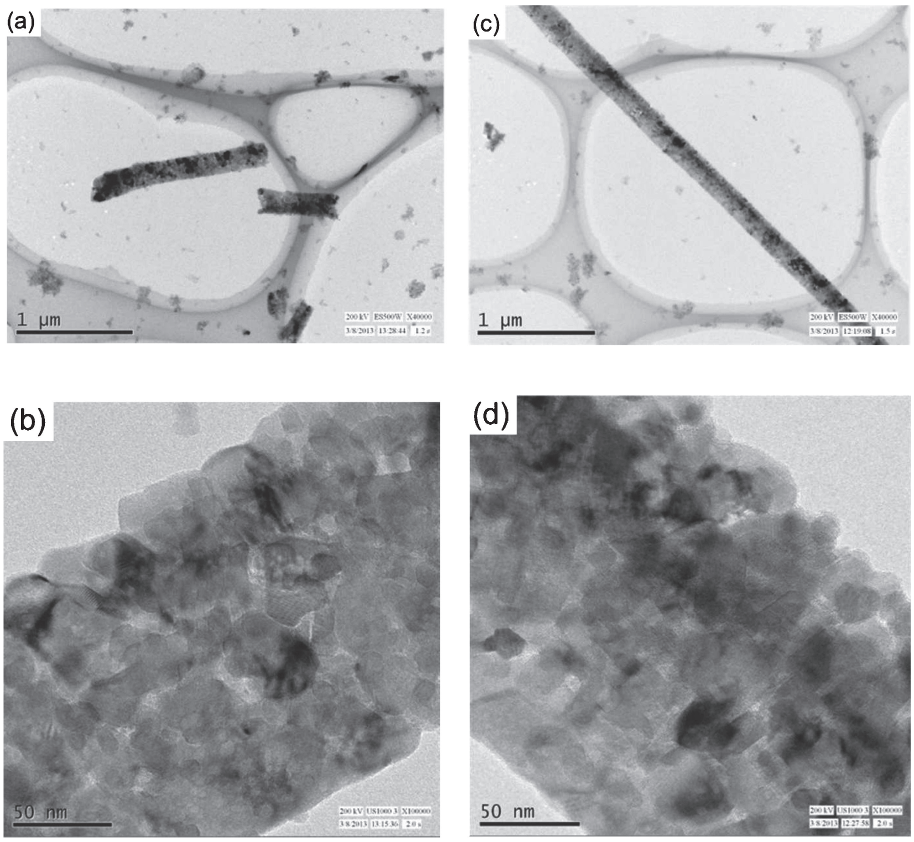

Fig. 5. TEM images of (a) (b) nanorods and (c) (d) nanowires prepared by immersion setting (IS) and vacuum and drop setting (VDS), respectively.

1 µm and diameter of ~200 nm were observed. The diameter of the nanorods was in good agreement with the hole diameter of the AAO template. In Fig. 3(b), TiO_2 nanowires with the maximum length of 60 µm and diameter of ~200 nm were observed. The maximum length (60 µm) of nanowires was exactly in accord with the thickness of AAO template (60 µm). These results demonstrate that the length of 1-D nano TiO_2 can be controlled only by changing the sample setting (whether IS or VDS). For the immersion setting, only the vicinity of AAO-surface was filled with Ti-precursor solution, and then, the precursor solution was changed into TiO_2 nanorods. A certain amount of nanoparticles other than nanorods were also found for the IS; the precursor solution remained on the surface of AAO probably changed into these nanoparticles. For the vacuum and drop setting, the precursor solution penetrated into AAO holes. The length deviation for IS and VDS can be attributed to the penetration depth of the precursor solution (**Fig. 4**). TEM observation revealed that the nanorods and nanowires were composed of fine TiO_2 particles (ca. 10–20 nm) (**Fig. 5**).

4. Conclusions

In this study, we have synthesized well-defined TiO_2 nanorods or nanowires using AAO-template method. Just by changing fabrication procedure, nanorods and nanowires were easily fabricated. This method is very simple and effective to control the length of polycrystalline nanomaterials, and will be applicable to other systems. Further controls, e.g., wettability control of precursor and AAO template, and more precise control of the pressure, will be effective to obtain more uniform 1-D nanomaterials.

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