Formation of vertically grown 1D TiO$_2$ nanorods on the surface of Al$_2$O$_3$/Ti composites by simple heat treatment and their photocatalytic performance

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A simple method was used to form one-dimensional (1D) TiO$_2$ nanorod arrays on the surfaces of hot-pressed Ti-dispersed Al$_2$O$_3$ composites by heating. After heating below 600°C, the Ti surface morphologies had changed significantly, while the Al$_2$O$_3$ surfaces remained unchanged. After heating for 5 h above 500°C, vertically grown nanorods were observed on the surfaces of Ti grains among Al$_2$O$_3$/Ti composites, which exhibited a crystalline phase of rutile-type TiO$_2$ doped with a small quantity of aluminum. Nanorod formation was believed to be due to Ti diffusion and its acceleration by Al incorporation. The photocatalytic activity of the heated Al$_2$O$_3$/Ti composites was verified by rhodamine B degradation under ultraviolet light irradiation, although the oxide fraction on the composites was small. The activity was enhanced by 1D TiO$_2$ nanorod growth on the composite surface.

Key-words : 1D TiO$_2$ nanorod, Al$_2$O$_3$/Ti composite, Heat treatment, Photocatalytic activity

Nanostructured TiO$_2$ has attracted widespread attention with respect to its potential applications in photocatalysis, sensors, water splitting, and photovoltaic cells.$^{1–5}$ The morphology and structure of TiO$_2$ significantly affects its properties. One-dimensional (1D) TiO$_2$ nanostructures such as nanotubes, nanorods, and nanowires have been extensively investigated due to their unique properties, including direct electrical pathways, good charge transport, high mechanical strength,$^6$ excellent chemical stability, and high refraction index, together with their low production cost.$^7–9$ Additionally, it was reported that 1D TiO$_2$ nanorod arrays prolong the life of photogenerated charge carriers and thus enhance their photocatalytic activity.$^{10}$

Several methods have been developed to form TiO$_2$ nanorod arrays on fluorine-doped tin oxide (FTO) glass substrates,$^2$ polymer substrates,$^{11}$ and metal sheets.$^{12}$ These techniques involve Ti substrate oxidation,$^{13}$ solvothermal processes,$^{14}$ template-assisted processes, sol–gel reactions$^{15,16}$ and hydrothermal synthesis.$^{17–20}$ Shen et al.$^2$ prepared TiO$_2$ nanorod arrays on FTO substrates via a hydrothermal process and characterized their photodegradation efficiency with respect to rhodamine B (RhB) under visible light irradiation.

As TiO$_2$ can be obtained by oxidizing Ti metal, TiO$_2$ nanorod formation by simple heating in air or oxygen on a suitable substrate has also been explored. Peng and Chen$^{3}$ successfully synthesized TiO$_2$ nanorods on a titania substrate by oxidation at 850°C, employing organo-metallic compounds as oxygen sources. They suggested that Ti diffusion at a higher temperature was an effective factor in forming the nanorods.

We recently reported fine Ti particles dispersed in Al$_2$O$_3$ ceramic matrix composites (Al$_2$O$_3$/Ti) via in-situ decomposition and sintering of ball-milled TiH$_2$ and Al$_2$O$_3$ mixtures, which exhibited excellent mechanical and electrical properties.$^{21}$ During sintering, TiH$_2$ decomposed to Ti metal particles, while Al$_2$O$_3$ also decomposed, and the resultant oxygen and/or aluminum diffused into Ti. Furthermore, we recently formed nanoporous structures consisting of a nanosheet-like titane compound by chemically treating Al$_2$O$_3$/Ti composites at low temperature. Subsequent heating converted nanoporous titane to TiO$_2$ nanoplates or short nanorods, which exhibited photocatalytic properties.$^{22}$ However, these nanoplates/nanorods formed randomly on the composite surface, and the desired long and well-grown nanorod array was not achieved.

In this work, we attempted to generate TiO$_2$ nanorod arrays on the surfaces of Al$_2$O$_3$/Ti composites via simple heating for photocatalytic applications. When the Al$_2$O$_3$/
Ti ceramic-based composite displayed photocatalytic properties, it offered crucial advantages over metal Ti, including high bending strength, improved wear behavior, high-temperature oxidation, corrosion resistance, good chemical stability, and a low elastic modulus.\textsuperscript{23)}

To form 1D TiO\textsubscript{2} nanorods on the surfaces of Al\textsubscript{2}O\textsubscript{3}/Ti composites, the effects of various heating conditions on nanorod formation were studied. These included the heating temperature and time, and the Al\textsubscript{2}O\textsubscript{3} and Ti contents in the composite substrates. The photocatalytic degradation efficiency with RhB was investigated for heat-treated Al\textsubscript{2}O\textsubscript{3}/Ti composites to endow these with multiple functions as well as their excellent mechanical properties.

The raw materials used to prepare Al\textsubscript{2}O\textsubscript{3}/Ti composites were titanium hydride powder (TiH\textsubscript{2}, 5–10 \textmu m, \geq 99\%, Kojundo Chemical Laboratory Co., Ltd., Sakado, Japan) and \alpha-Al\textsubscript{2}O\textsubscript{3} powder (0.2 \textmu m, AKP-53; Sumitomo Chemicals Co., Ltd., Japan). Mixtures of these (20, 50, 80, and 100 vol\% Ti) were prepared by ball-milling for 24 h, followed by hot-press sintering (HPS) with an applied pressure of 30 MPa at 1,500\degree C for 1 h in Ar.\textsuperscript{21)} After cutting and polishing, samples were heated at 400, 500, and 600\degree C for 1, 2, 3, and 5 h in an air flow at a heating rate of 5\degree C/min to form TiO\textsubscript{2} nanorods on the surface.

The surface structures of the samples were observed by field-emission scanning electron microscopy (FE-SEM; SU9000, Hitachi, Japan) with energy dispersive X-ray (EDX) spectroscopy (Horiba, Japan). Phases were identified by X-ray diffraction (XRD; D8 Advance, Bruker Ltd., USA) with Cu K\alpha radiation at 40 kV and 40 mA.

The photocatalytic activity of heat-treated composites was investigated as follows: a hot-pressed sample was divided into four plates (15 x 15 x 1.5 mm) and heated (400–600\degree C, 1–5 h). After immersing the four pieces in RhB solution (30 mL, 5 mg/L) and soaking in the dark for 1 h, these were irradiated using a ultraviolet (UV) light source (Supercure-204S, San-EI Electric, Japan) under ambient conditions. RhB absorbed light at 553 nm following a change in its concentration.

| Table 1. Chemical compositions of the nanorods formed on the surface of the Al\textsubscript{2}O\textsubscript{3}/20 vol\% Ti composite, measured by EDX spectroscopy [positions shown in Fig. 1(c)] |
|---|---|---|---|
| Point | Elements (at.\%) | Relative ratio of O/Ti | Relative ratio of O/[Ti + Al] |
| 1 | 19.7 | 7.6 | 72.6 | 3.68 | 2.66 |
| 2 | 18.8 | 9.5 | 71.6 | 3.81 | 2.53 |
| 3 | 25.2 | 7.9 | 66.9 | 2.65 | 2.02 |

The microstructure of the sintered Al\textsubscript{2}O\textsubscript{3}/20 vol\% Ti composite consisted of dispersed 2–5 \textmu m Ti particles. These were partially isolated and partially connected in the Al\textsubscript{2}O\textsubscript{3} matrix, as reported in our previous study.\textsuperscript{21)} The surface morphology of the heated samples is shown in Fig. 1. After heating at 400\degree C, fine nanoscale particles formed on the surfaces of the dispersed Ti grains, which were observed as white regions in the SEM images. When the temperature was increased to 500\degree C, the particle size increased while remaining on the nanoscale level. After heating at 600\degree C for 5 h, a well-grown nanorod structure was observed. EDX spectroscopy indicated that the nanorods consisted of Ti and O with a small quantity of Al (Table 1). The relative atomic ratios O/Ti and O/[Ti + Al] were above 2, indicating that the nanorods were TiO\textsubscript{2}, although a small quantity of Al was doped in the TiO\textsubscript{2}.

Figure 2 shows the surface morphology variation with time for the Al\textsubscript{2}O\textsubscript{3}/Ti composite heated at 600\degree C. In the sample heated for 1 h, nanoparticles appeared on the Ti surface. After heating for 2 h, 1D nanorods started to form. After heating for 3 h, the Ti surface was almost completely covered with nanorods, many of which grew vertically toward the Ti substrates, although some particles remained. After heating for 5 h, well-aligned nanorod arrays formed over the whole Ti surface, while no change was observed in the Al\textsubscript{2}O\textsubscript{3} matrix region. As well as the well-ordered nanorod arrays, randomly grown nanorods were observed as minor structures as shown in Figs. 2(e) and 2(f).
Figure 3 shows that, before heating, the composite comprised $\alpha$-Al$_2$O$_3$ and $\alpha$-Ti. These two major phases were retained even after heating to 600°C; however, rutile-type TiO$_2$ was identified after heating above 500°C.

Figure 4 shows SEM images of composites with various Al$_2$O$_3$/Ti fractions (0/100, 20/80, and 50/50 vol%) heated at 600°C for 5 h. No nanorods were observed on the surface of pure Ti, while rod-like structures were observed on the surfaces of the Al$_2$O$_3$/50 vol% Ti and 80 vol% Ti composites. However, the nanorods were present in relatively lower quantities and were smaller [Figs. 4(b) and 4(c)] compared to those of the 20 vol% Ti composites.

To understand the TiO$_2$ nanorod formation, various factors must be considered. These include the oxidation dynamics and reaction kinetics of Ti, Al, and O diffusion from the Al$_2$O$_3$ matrix, Ti in the oxidized surface, the oxygen concentration in the surface growing region, and the crystalline characteristics of the dispersed Ti phase. During sintering of the composites, Al and O diffused from Al$_2$O$_3$ to the Ti particles and reacted to form oxygen dissolved in Ti and TiAl$_2$O$_5$, as expressed by the following equations:

1. $\text{Al}_2\text{O}_3 \rightarrow 2\text{Al} + 3/2 \text{O}_2$
2. $\text{Ti} + 3/2 \text{O}_2 \rightarrow 3\left[\text{O}\right]_{\text{Ti}}$
3. $\text{Ti} + 2\text{Al} + 5/2 \text{O}_2 \rightarrow \text{TiAl}_2\text{O}_5$

where $\left[\text{O}\right]_{\text{Ti}}$ represents active oxygen dissolved in titanium. The free energy changes $\Delta G$ for Eqs. (2) and (3) are $-1,279.2$ and $-1,753.6$ kJ/mol, respectively, at 1,500°C. When the composites were heated below 600°C for this surface modification, no significant reactions occurred between Al$_2$O$_3$ and Ti, except for Ti metal oxidation. XRD analysis showed no new phases apart from TiO$_2$. No peaks were observed for the TiAl$_2$O$_5$ phase in this study due to its minute quantity. However, its formation in the Al$_2$O$_3$/Ti composite is discussed in our previous report.

When the Al$_2$O$_3$/Ti composite was heated, an oxide film was initially formed on the Ti surface. The heating temperature significantly affects the surface morphology due to changes in the kinetics. At a temperature below 500°C, Ti diffusion was slow compared to Ti oxidation by O$_2$. Consequently, the Ti surface was oxidized to form only nanoparticles. Increasing the heating time enhanced oxygen and aluminum diffusion from the Al$_2$O$_3$ matrix to the Ti metal phase, promoting Ti oxidation and forming nanorods. At a higher temperature, the diffusion of chemical species, particularly Ti and O, was enhanced, and the TiO$_2$ crystals grew into nanorods.

Additionally, the Ti dispersed in the Al$_2$O$_3$/Ti composite contained imperfections such as defects, strains, and oxygen and aluminum impurities, which were introduced.
during processing.\textsuperscript{21}) The composite with 20 vol\% Ti was expected to have the highest concentration of imperfections, and these contributed to the increased reactivity and nanorod formation.

As mentioned earlier, Peng and Chen\textsuperscript{13}) showed that Ti diffusion was key to TiO$_2$ nanorod growth. In this study, faster Ti diffusion through the grain boundaries and/or surfaces of nanocrystalline TiO$_2$ particles with longer heating times and higher temperatures is probably the main reason for the growth of TiO$_2$ nanorod arrays. Also, in this study, nanorods were obtained at a much lower temperature (600°C) than that of 850°C reported by Peng et al.\textsuperscript{13}) This low formation temperature can be ascribed to the presence of Al$_2$O$_3$ and resultant Al and O impurities in the Ti phase in the composites.\textsuperscript{21}) As shown in Fig. 1 and Table 1, the nanorods contained not only Ti and O but also a small quantity of Al. When the composites were reheated in air, Al in the Al$_2$O$_3$ matrix phase as well as diffused Al present in the Ti or TiAl$_2$O$_5$ phases should promote further diffusion in the TiO$_2$ phase, accelerating nanorod growth.

Based on the phase diagram between Al$_2$O$_3$ and TiO$_2$\textsuperscript{29)} and previous reports, the solubility of Ti in Al$_2$O$_3$ and that of Al in TiO$_2$ were minute. The solubility limit of Al in TiO$_2$ was approximately 2.5 at\%\textsuperscript{29)} while that of TiO$_2$ in Al$_2$O$_3$ was 0.27 wt\% (0.11 at\% of Ti to Al) above 1,300°C.\textsuperscript{30,31)} In the composites in this study, the Al concentration in TiO$_2$ nanorods should be low, although Al was detected in the nanorods (Table 1). Additionally, the O/Ti and O/[Ti + Al] ratios were above 2; this can be partially explained by the presence of the TiAl$_2$O$_5$ phase in the composites. It should be mentioned that errors cannot be neglected in measuring the TiO$_2$ phase in a very small fraction of the surface.

The results shown in Fig. 4 confirm that Al$_2$O$_3$ is essential for nanorod formation. In the absence of Al$_2$O$_3$ (pure Ti metal), no nanorods were formed on the surface [Fig. 4(a)]. When the Ti content was raised to 80 vol\%, a small quantity of Al$_2$O$_3$ hindered nanorod formation, although some rod-like structures were seen [Fig. 4(c)]. These results confirmed that Al played an important role in TiO$_2$ nanorod formation between 500 and 600°C. As mentioned earlier, the reaction between Al$_2$O$_3$ and Ti, leading to the formation of TiO and TiAl$_2$O$_5$ phases, occurred during sintering. However, heating below 600°C in air resulted in the reaction between Al$_2$O$_3$ and Ti being negligible, while simple oxidation of Ti to TiO$_2$ was key to the formation of TiO$_2$ phases in the composite.

Figure 5 shows photocatalytic RhB degradation under UV light for heat-treated Al$_2$O$_3$/20 vol\% Ti composites. The degradation efficiency increased with the heating temperature. After exposure to UV light for 12 h, the highest degradation efficiency with respect to RhB was about 18\% for the sample heated at 600°C. There was no significant difference between the photocatalytic performances of samples heated at 500 and 600°C.

It is noteworthy that the amount of photocatalytic oxide phase was minute in the composites. The quantity of TiO$_2$ calculated from the weight change was approximately 0.11 mg/plate after heating to 600°C in air for a sample plate $15 \times 15 \times 1.5$ mm with an initial weight of 1.4 g/plate.

Changing the heating temperature significantly altered the morphology, which could be due to the Al$_2$O$_3$/20 vol\% Ti composites having an increased surface area, as shown in Fig. 1. This explains the increased photocatalytic activity as the heating temperature increased from 400 to 600°C. The surface morphology change from nanoparticlles at 400°C to nanorods at 600°C is accompanied by an increase in the surface area. When the samples were heated at 500°C, a rutile phase appeared, and the quantity of rutile-type nanorods increased at 600°C (Fig. 2). Both the large surface area resulting from the 1D nanostructure and the existence of rutile are considered to promote the high photocatalytic activity in the present study.

Thermally and hydrothermally grown rutile nanorods often had a (001) growth direction, and the corresponding nanorod wall consisted of [110] planes, which formed the active surface for photocatalytic reactions.\textsuperscript{13,32)} While a detailed analysis of rutile nanorods is needed to further investigate the high photocatalytic activity in this study, the crystallized rutile nanorods on the Al$_2$O$_3$/Ti composite surfaces are clearly central to this.

To summarize, this study demonstrates, for the first time, the formation of vertically aligned rutile-type 1D TiO$_2$ nanorod arrays on the surfaces of Al$_2$O$_3$/Ti composites via simple heating. After heating for 5 h, the Ti surface was completely covered with nanorod arrays. The formed nanorods exhibited improved photocatalytic activity, although the total volume of the TiO$_2$ phase in the surfaces of the ceramic-metal composites was relatively small. With the TiO$_2$ nanorod formation, further addition of novel functions to Al$_2$O$_3$/Ti composites, which were already reported to exhibit multifunctionality with enhanced toughness and good electrical properties, was achieved. This surface modification to form TiO$_2$ nanorods also indicates that the present composites may be employed as photochemically functionalized ceramic-based components and various electrodes, such as in solar cells, and chemical- and photosensors, due to their multifunctionality.
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