# Anatase Sol Prepared from Peroxotitanium Complex Aqueous Solution Containing Niobium or Vanadium

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Niobium- or vanadium-doped anatase sols were prepared by hydrothermal treatment of 0.1 mol/dm<sup>3</sup> peroxotitanium complex aqueous solutions dissolving 0–10 mol% niobium or vanadium at 100°C for 8 h. Niobium-doping caused the increase of lattice constants of anatase and the shape change of anatase crystal from spindle-like to cubic-like structure, but no change of the optical absorbance. Vanadium-doping caused the decrease of lattice constant of *c*-axis, the miniaturization of anatase crystal and the increase of optical absorbance at the wavelength from 350–700 nm.

## I. Introduction

 $T_{102}$  is useful for solar cells,<sup>1</sup> gas sensors,<sup>2,3</sup> photocatalysts,<sup>4</sup> and more. In particular, TiO<sub>2</sub> film has been studied extensively by the sol–gel method<sup>5</sup> and solid-state reaction.<sup>6</sup> In recent years, much importance has been given to the studies of niobium- or vanadium-doped TiO<sub>2</sub><sup>7,8</sup> prepared by the coprecipitation method with organic metals and chlorides as starting materials. On the other hand, it is well-known that H<sub>2</sub>O<sub>2</sub> forms peroxotitanium complex with titanium.<sup>9-11</sup> It was also reported that anatase sol, containing well-dispersed anatase crystallite surface modified with peroxo groups, was obtained by autoclaving peroxotitanium complex aqueous solution or peroxotitanium hydrate suspension at 100°C for 6 h.<sup>12-14</sup> The peroxotitanium complex aqueous solution can be prepared by adding aqueous H<sub>2</sub>O<sub>2</sub> into freshly prepared and well-washed titanic acid<sup>12</sup> or peroxotitanium hydrate.<sup>14</sup> The peroxotitanium complex aqueous solution and the anatase sol contain some ammonia as a stabilizer and are neutral or weak base in pH.

If a chemically homogeneous mixture of the peroxotitanium complex aqueous solution and transition metal ions can be obtained, it may become possible to prepare metal-doped anatase sol by the hydrothermal reaction at low temperature, and it is expected that the application will spread as the form of thin films. However, the homogeneous mixture cannot be performed because insoluble precipitate is deposited by mixing transition metal ions to the peroxotitanium complex aqueous solution. This phenomenon is explained as polymerization by the bridge construction reaction between peroxotitanium complexes through transition metal ions in an instant. Because niobium or vanadium are known to form peroxo-complexes,<sup>15</sup> the mixture is expected to mix homogeneously with peroxotitanium complex aqueous solution.

In this study, the peroxotitanium complex aqueous solution containing a peroxo-complex of niobium or vanadium was prepared, and then niobium- or vanadium-doped anatase sols were synthesized by hydrothermal treatment. Moreover, the optimal

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concentration of ammonia for the crystallization to anatase was also determined.

## **II. Experimental Procedure**

Titanium powder (>98% of purity, Wako Pure Chemical Industries, Osaka, Japan), niobium powder (99.5% of purity, Wako Pure Chemical Industries), and vanadium turnings (99.5% of purity, Wako Pure Chemical Industries) were used as starting materials. First, 0.01 mol titanium powder was dropped in the mixed solution of ammonia water (3 mol/dm<sup>3</sup>) 15 mL and H<sub>2</sub>O<sub>2</sub> solution (~30 mass%) 65 mL, and dissolved completely over several hours. Next, ammonia concentration in the solution was



Fig. 1. FT-IR spectra of the liquids prepared by heating peroxotitanium complex aqueous solution at 100°C for 8 h with different ammonia concentrations.



Fig. 2. XRD patterns of the liquids prepared by heating peroxotitanium complex aqueous solution at  $100^{\circ}$ C for 8 h with different ammonia concentrations.

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50nm

Fig. 3. TEM photographs of niobium- or vanadium-doped anatase sol: (a) nondoped, (b) Nb 2 mol%, (c) Nb 5 mol%, (d) Nb 10 mol%, (e) V 2 mol%, (f) V 5 mol%, (g) V 10mol%.

reduced by following methods; adding H<sup>+</sup>-type cation-exchange resin (Amberlite IR118, Organo, Japan) to the dissolved titanium solution while stirring slowly until pH is set to  $\sim$ 5, separating the resin, and carrying out ultrasonic treatment to decompose excess

 $H_2O_2$  until pH increased to  $\sim 7$ . This ion-exchange process was repeated three to four times, and then a transparent peroxotitanium complex aqueous solution of 0.1 mol/dm<sup>3</sup> was obtained. The concentration of ammonia was adjusted to 0.0063, 0.014, 0.021,



Fig. 4. Lattice constants of niobium- or vanadium-doped anatase.



Fig. 5. Optical absorbance spectra of dried vanadium-doped anatase sol.

0.028, 0.036, and 0.043 mol/dm<sup>3</sup>. The translucent anatase sol was obtained by heating the prepared solutions in an airtight container at  $100^{\circ}$ C for 8 h. Niobium- or vanadium-doped anatase sols (dopant ratio: 0, 2, 5, and 10 mol%) were prepared by the same method, but the ammonia concentration was 0.01mol/dm<sup>3</sup>.

The anatase sols were characterized by powder X-ray diffractometry (XRD; Geigerflex RAD-B, Rigaku, Tokyo, Japan), BET specific surface meter (Auto-sorb 1, Yuasa Ionics, Osaka, Japan), FT-IR spectrophotometry (Model FT/IR-5300, Jasco, Tokyo, Japan), UV-visible spectrophotometry (Model U-3100, Hitachi, Tokyo, Japan), transmission electron microscopy (TEM; JEM-2010, JEOL, Tokyo, Japan). UV-visible light reflection spectra were measured for the films, which were prepared with the powder and little water so that it might be 2 mg/cm<sup>2</sup> on a glass. The concentration of ammonia was measured by the colorimetry of indophenol with the light wavelength of 630 nm.

#### III. Results and Discussion

## (1) Optimal Ammonia Concentration for Crystallization

FT-IR spectra of the liquids prepared by heating peroxotitanium complex aqueous solution at 100°C for 8 h with different ammonia concentrations are shown in Fig. 1. In the case of 0.021 mol/dm<sup>3</sup> and more of ammonia concentration, the infrared absorption resulting from free peroxide (O-O, bond order = 1) stretching mode was detected at 890 cm<sup>-1.16</sup> It is suggested that the peroxotitanium complex remained after heating by a stabilizing effect of ammonia. The broad peaks at 3200–3400 cm<sup>-1</sup> and a clear peak at 1630 cm<sup>-1</sup> are attributed to water molecules. A peak at 1400 cm<sup>-1</sup> is due to the stretching vibration of N-H bonds in ammonia. XRD patterns are shown in Fig. 2. In the case of <0.014

mol/dm<sup>3</sup>, only anatase phase was detected. Therefore, it is necessary to make ammonia concentration into  $<0.014 \text{ mol/dm}^3$  to crystallize smoothly to anatase phase. However, when ammonia concentration was decreased to  $0.0063 \text{ mol/dm}^3$  or less, the peroxotitanium complex solution became too high in viscosity to obtain a stable anatase sol and finally solidified as jelly-like. Consequently, it turned out that ammonia concentration in the range of  $0.0063-0.014 \text{ mol/dm}^3$  is suitable for the preparation of anatase sol. In the next experiments, ammonia concentration was performed as  $0.01 \text{ mol/dm}^3$ .

### (2) Properties of Niobium- or Vanadium-Doped Anatase Sol

The peroxotitanium complex aqueous solutions dissolving niobium or vanadium crystallized only to anatase phase by heating at 100°C for 8 h. The anatase particles dispersed homogeneously in the solvent. These translucent anatase sols were stable for a long time. TEM photographs of anatase particles are shown in Fig. 3. In the case of nondoping, there were spindle-like and arrowhead-like anatase crystals. The aspect ratio of anatase particle decreased gradually with the addition of niobium, and the shape of crystals turned out to be cubic at 10 mol% niobium. According to electron diffraction analysis, the square faces of crystals were anatase (101). The crystal size and the aspect ratio of anatase crystals decreased gradually with the addition of vanadium. The size was 5-8 nm at 10 mol% vanadium. The specific surface area of nondoped sol was 165  $m^2/g$ , and decreased gradually with the addition of niobium. However, the specific surface area increased dramatically up to 210 m<sup>2</sup>/g even at 2 mol% vanadium, and it didn't increase any more with further additions.

Lattice constants of niobium- or vanadium-doped anatase are shown in Fig. 4. Although the lattice constants of nondoped anatase closed to the reference values, they increased gradually with the addition of niobium. In the case of the addition of vanadium, the lattice constant of the c-axis decreased with the addition, but that of the *a*-axis did not change entirely. UV-visible light reflective spectra of dried vanadium-doped anatase sols are shown in Fig. 5. The optical absorption increased with the addition of vanadium at the wavelength from 350 nm to a visible light region, but there was no change with the niobium addition. It has been reported that  $Nb_2O_5$  forms an interstitial solid solution >0.6 mol% at 700°C with the increase of lattice constants.<sup>17</sup> It is suggested in this study that niobium formed an interstitial solid solution in anatase. It was also suggested that small  $V^{5+}$  ion (0.054 nm) substituted for the Ti<sup>4+</sup> ion (0.061 nm), and the lattice constant was reduced by the size difference. However, the amounts of substitutions could not be clarified.

#### IV. Conclusions

We synthesized peroxotianium complex aqueous solutions containing niobium or vanadium using the metals as starting materials, and niobium- or vanadium-doped anatase sols were obtained by hydrothermal treatment at 100°C. Moreover, the optimal concentration of ammonia for the crystallization to anatase phase turned up. It should be emphasized that the peroxotitanium complex aqueous solution is highly stable at a pH of  $\sim$ 7, and therefore has potential applications in inexpensive and convenient syntheses of metal-doped anatase sols for industrially important products.

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