

# A New Water-Soluble Ammonium Citratoperoxotitanate as an Environmentally Beneficial Precursor for TiO<sub>2</sub> Thin Films and RuO<sub>2</sub>/BaTi<sub>4</sub>O<sub>9</sub> Photocatalysts

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Received October 25, 2001

Titanium compounds have a broad range of industrial applications. They are widely used in the manufacturing of ferroelectric materials, semiconductors, or photocatalysts for environmental waste removal. Handling titanium precursor compounds is difficult because the solutions react readily with atmospheric moisture, making their use inconvenient and rather costly. A major goal in this field is, therefore, to develop a new nontoxic titanium compound that is soluble in neutral water. We have recently prepared such a crystalline compound, ammonium citratoperoxotitanate(IV), with a chemical formula of (NH<sub>4</sub>)<sub>8</sub>[Ti<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>O<sub>7</sub>)<sub>4</sub>(O<sub>2</sub>)<sub>4</sub>]·8H<sub>2</sub>O, that dissolves in pure water and possesses high stability against hydrolysis in a broad range of pH.<sup>1</sup> The tight coordination of titanium in the [Ti<sub>4</sub>(C<sub>6</sub>H<sub>4</sub>O<sub>7</sub>)<sub>4</sub>(O<sub>2</sub>)<sub>4</sub>]<sup>8-</sup> anion is thought to be responsible for the high stability of this compound against hydrolysis because it creates a steric obstacle for the nucleophilic substitution.<sup>1</sup> We thus anticipate that the new compound will be particularly useful in a wide range of applications including water-based solutions to coat substrates of any shape and/or as a potential precursor for oxide ceramics synthesis via aqueous solution routes.

Here, we report the applicability of the new compound as a water-soluble precursor for synthesis of Ti-based oxide materials by fabricating TiO<sub>2</sub> thin films on Si wafer substrates and preparing RuO<sub>2</sub>/BaTi<sub>4</sub>O<sub>9</sub> photocatalytic nanocomposites.<sup>2,3</sup> The latter system is the one quite suitable for testing the feasibility of the new aqueous titanium precursor because the preparation of pure single-phase BaTi<sub>4</sub>O<sub>9</sub> at temperatures below 1000 °C is a difficult task<sup>4–9</sup> and because the photocatalytic

activity of a composite material, RuO<sub>2</sub>/BaTi<sub>4</sub>O<sub>9</sub>, with respect to decomposition of water into H<sub>2</sub> and O<sub>2</sub> is strongly depressed by the presence of impurities.<sup>10</sup>

Ammonium citratoperoxotitanate was obtained in a solid form according to the procedures described in our previous paper.<sup>1</sup> A thin film of TiO<sub>2</sub> on a <111>Si wafer substrate was obtained by a dip-coating method using an aqueous solution of ammonium citratoperoxotitanate with subsequent annealing in air at 500 °C for 30 min. For the synthesis of BaTi<sub>4</sub>O<sub>9</sub>, we used an aqueous solution containing ammonium citratoperoxotitanate and an excess of citric acid (CA) with CA/Ti = 10/1. Barium carbonate (BaCO<sub>3</sub>) with Ba:Ti = 1:4 was added into this solution. After complete dissolution of BaCO<sub>3</sub>, the mixture was heated on a hot plate set at 300 °C for several hours to produce a puffy gel, which was further heat-treated at 450 °C to obtain an amorphous powder precursor for BaTi<sub>4</sub>O<sub>9</sub>. The powder precursor was calcined at 700 and 800 °C for 2 h in air.

Photocatalytic composite materials of RuO<sub>2</sub>/BaTi<sub>4</sub>O<sub>9</sub> were prepared as follows. The powder of BaTi<sub>4</sub>O<sub>9</sub> prepared at 800 °C was suspended into an aqueous solution containing RuCl<sub>3</sub> (1 wt % of Ru relative to BaTi<sub>4</sub>O<sub>9</sub>) and the suspension was stirred for 4 h at ≈70 °C until most of the water had evaporated. The resulting mass was dried at 100 °C for 12 h. The Ru-impregnated BaTi<sub>4</sub>O<sub>9</sub> was heat-treated at 500 °C for 2 h under flowing H<sub>2</sub>/N<sub>2</sub> gas (H<sub>2</sub> 2% + N<sub>2</sub> 98%), followed by oxidation at 475 °C under flowing air for 7 h to obtain RuO<sub>2</sub>/BaTi<sub>4</sub>O<sub>9</sub>.

With respect to phase identification for our TiO<sub>2</sub> thin film on a <111>Si substrate, X-ray diffraction (XRD) measurements gave no clear information because of the strong Si(111) peak at 2θ = 28.44° that masks the strongest reflections from TiO<sub>2</sub>. For this reason, we utilized Raman spectroscopy as a means for phase identification. Figure 1 shows a Raman spectrum of our TiO<sub>2</sub> thin film obtained by the dip-coating method on a <111>Si wafer substrate, confirming the formation of anatase modification of TiO<sub>2</sub>. As one can see from a SEM photograph in Figure 1, the fabricated TiO<sub>2</sub> film is dense and homogeneous and has a fine-grained microstructure with a grain size of about 40 nm. The thickness of the film with one dip coating was about 100 nm. The photocatalytic activity of the thus-fabricated TiO<sub>2</sub> films was proved by bleaching of organic dye painted onto the film upon its exposure to sunshine.

The XRD patterns of powders obtained after calcining the amorphous precursor for BaTi<sub>4</sub>O<sub>9</sub> in air at 700 and 800 °C for 2 h are shown in Figure 2 in a 2θ range of 10–80°. The powder precursor calcined at 700 °C was primarily amorphous, as shown by a broad diffuse

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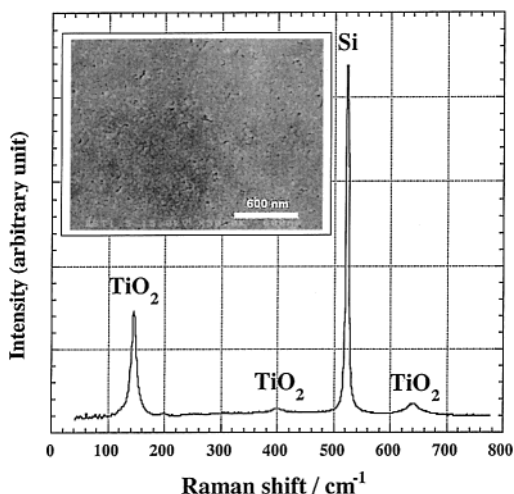
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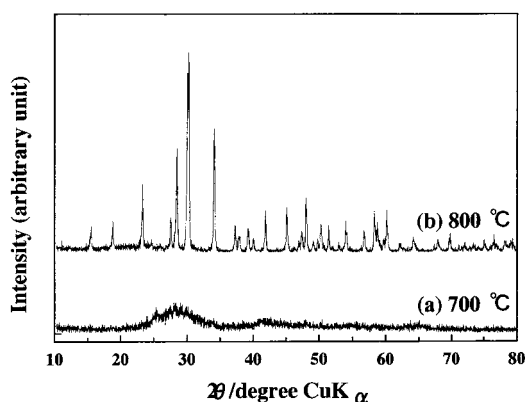
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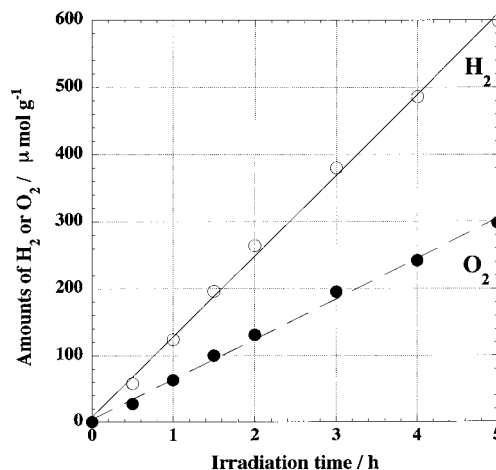


**Figure 1.** Raman spectrum of a  $\text{TiO}_2$  thin film on a  $\langle 111 \rangle \text{Si}$  substrate heat-treated for 30 min at  $500^\circ\text{C}$ . Inset shows a SEM photograph of the surface of the same  $\text{TiO}_2$  thin film on the  $\langle 111 \rangle \text{Si}$  substrate.



**Figure 2.** X-ray diffraction patterns of products obtained by heating the powder precursor in air for 2 h at  $700^\circ\text{C}$  (a) and  $800^\circ\text{C}$  (b).

scattering in the XRD pattern in Figure 2a. Crystallization has occurred during the calcination of the powder precursor in air at  $800^\circ\text{C}$  for 2 h (Figure 2b). All the well-defined peaks in the XRD pattern of Figure 2b exhibited a pure orthorhombic phase of  $\text{BaTi}_4\text{O}_9$ , in good agreement with the XRD pattern reported for this compound by Phule and Risbud.<sup>8</sup> It is worthwhile to recall here that  $\text{BaTi}_4\text{O}_9$  is very difficult to be synthesized as a single phase at temperatures below  $1000^\circ\text{C}$ . For instance,  $\text{BaTi}_4\text{O}_9$  has been synthesized by the conventional solid-state reaction route, which involves mixing  $\text{BaCO}_3$  and  $\text{TiO}_2$ , followed by repeated cycles of grinding and firing at high temperatures ( $1000$ – $1300^\circ\text{C}$ ).<sup>4–7</sup> The sol–gel synthesis of  $\text{BaTi}_4\text{O}_9$  using metal alkoxides has been reported by several groups.<sup>8,9</sup> However, gels derived from alkoxide precursors are transformed into phases such as  $\text{BaTi}_5\text{O}_{11}$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ , or  $\text{BaTi}_2\text{O}_5$  at temperatures below  $900^\circ\text{C}$ . Calcination at  $1100^\circ\text{C}$ <sup>8</sup> or  $1300^\circ\text{C}$ <sup>9</sup> was necessary to obtain crystalline single-phase  $\text{BaTi}_4\text{O}_9$ . The reported multiphase char-



**Figure 3.** Photocatalytic decomposition of water ( $\circ$ ,  $\text{H}_2$ ;  $\bullet$ ,  $\text{O}_2$ ) by  $\text{RuO}_2/\text{BaTi}_4\text{O}_9$ .

acter of the sol–gel-derived products at temperatures below  $900^\circ\text{C}$  may be explained by different hydrolysis and condensation rates of titanium and barium alkoxides, which may result in localized enrichment of the titanium component in this case. Our success in lowering the crystallization temperature for  $\text{BaTi}_4\text{O}_9$  down to  $800^\circ\text{C}$  thus indicates an improved level of mixing of cations in the powder precursor derived from the newly developed aqueous solution route.

$\text{BaTi}_4\text{O}_9$  thus-prepared was subsequently converted to photocatalytic composite materials by modifying its surface with ultrafine particles of  $\text{RuO}_2$ , and the photodecomposition of water into  $\text{H}_2$  and  $\text{O}_2$  by  $\text{RuO}_2/\text{BaTi}_4\text{O}_9$  was carried out in a closed gas circulation reaction vessel under irradiation of light from a high-pressure Hg lamp operated at 100 W. Figure 3 shows the time dependence of  $\text{H}_2$  and  $\text{O}_2$  evolution of a  $\text{RuO}_2/\text{BaTi}_4\text{O}_9$  sample prepared at  $800^\circ\text{C}$  by our aqueous solution technique. It is clearly seen that  $\text{H}_2\text{O}$  was stoichiometrically decomposed into  $\text{H}_2$  and  $(1/2)\text{O}_2$ . Our  $\text{RuO}_2/\text{BaTi}_4\text{O}_9$  sample demonstrated a photocatalytic activity of  $\approx 120 \mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$  for the hydrogen gas evolution.

We applied stable water soluble titanium compound  $(\text{NH}_4)_8[\text{Ti}_4(\text{C}_6\text{H}_4\text{O}_7)_4(\text{O}_2)_4]\cdot 8\text{H}_2\text{O}$  for fabrication of  $\text{TiO}_2$  thin film and  $\text{RuO}_2/\text{BaTi}_4\text{O}_9$  composite in powder form for photocatalytic applications. The processing of each step of the sol–gel method was convenient and easy to control. The obtained samples demonstrated good photocatalytic activity. We would like to emphasize specially the use of water as a nontoxic and environmentally friendly solvent.

**Acknowledgment.** This work was financially supported by Nippon Sheet Glass Foundation for Materials Science and Engineering and by a Grant-in-Aid for Scientific Research (13450264).

CM011542Y