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Highly active BaTi₄O₉/RuO₂ photocatalyst by polymerized complex method

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A polymerized complex (PC) technique was utilized to prepare high-purity barium tetratitanate (BaTi₄O₉) fine powders at a low temperature (700 °C). BaTi₄O₉ *via* the PC route, combined with RuO₂, exhibited 2.4 times larger photocatalytic activities for the decomposition of water compared to those for a sample prepared by a solid-state reaction method. A considerably large surface area (~30 m²/g) of the BaTi₄O₉/RuO₂ powder *via* the PC route, when compared with ~5 m²/g for the solid-state reaction powder, was supposed to be one of the key factors responsible for the high photocatalytic activity observed. © 1996 American Institute of Physics. [S0003-6951(96)04740-7]

Apart from the suitable utilization of BaTi₄O₉ as a microwave dielectric resonator filter¹⁻⁵ in the electronic ceramic industry, the compound BaTi₄O₉ has recently received considerable attention as a new host catalytic material in combination with RuO₂ for stoichiometrically complete photodecomposition of water.^{6,7} The crystal structure of the host BaTi₄O₉ compound was reported by several groups,⁸⁻¹⁰ and it was shown to be isostructural with orthorhombic KTi₃NbO₉.¹¹ The BaTi₄O₉ compound is then characterized by the presence of the pentagonal-prism tunnel structure, which seems to play an important role in the emergence of the photocatalysis in BaTi₄O₉/RuO₂ as has been explained by Inoue *et al.*^{6,7} The significance of such photocatalytic activities in this new class of materials was discussed by the same authors^{6,7} from the following two standpoints: (i) the tunnel structure brings about a significantly large distortion of TiO₆ octahedra, possibly leading to efficient production of photoexcited charges, and (ii) it prevents RuO₂ particles from aggregating and growing into large particles.

One of the serious obstacles that blocks further substantial developments in the application of BaTi₄O₉/RuO₂ materials as photocatalysts with higher activities is the great difficulty in preparing a powder of the host BaTi₄O₉ compound with high surface areas. To obtain such active powders, processing temperatures must be set below ~700 °C so that the grain growth may not be very significant. BaTi₄O₉ has been synthesized by heat treatment of a mixture of BaCO₃ and TiO₂ at high temperatures (900–1300 °C) with repeated cycles of grinding and firing for the completion of the solid-state reaction.^{1,9,12} Alternatively, attempts to synthesize BaTi₄O₉ at lower temperatures have been carried out by sol-gel techniques using metal-alkoxides.^{13,14} However, gels derived from barium and titanium alkoxide precursors have

always produced strongly multiphase samples with impurities such as BaTi₅O₁₁, Ba₄Ti₁₃O₃₀, and BaTi₂O₅ after the heat treatment at temperatures below 900 °C.^{13,14} The BaTi₄O₉ phase did not crystallize from these gels until ~900 °C, and complete formation of BaTi₄O₉ could be achieved only at 1100 °C or 1300 °C.¹³ The primary problem in processing BaTi₄O₉ by these previously reported routes is the strong tendency to produce coarse and inhomogeneous powders with large grain sizes owing to the high-temperature heat treatments. This would in turn result in a host catalytic material with a relatively low activity due to the low surface area of the dense oxide powders. It is, therefore, necessary to develop a methodology for preparing fine powders of pure BaTi₄O₉ with high surface areas.

The principal aim of this letter is to report on a simple polymerized complex (PC) route, based on polyesterification between citric acid and ethylene glycol,^{15,16} that was successfully used to synthesize pure BaTi₄O₉ at 700 °C suitable for a host catalytic material with a high active surface. The photocatalytic activity for the decomposition of water in a BaTi₄O₉/RuO₂ material prepared *via* the PC route is compared with that in a sample prepared by the conventional solid-state reaction technique in order to demonstrate the potential advantage of the PC method in fabricating photocatalysts with higher activities.

The BaTi₄O₉ powders were synthesized by the PC method as outlined in Fig. 1. A 0.1 mol of titanium tetraisopropoxide (Ti[OCH(CH₃)₂]₄) was first dissolved into 4 mol of ethylene glycol (OHCH₂CH₂OH), and subsequently 1 mol of citric acid [(HOOCCH₂C(OH)(COOH)CH₂COOH)] was added in this solution. After achieving complete dissolution, 0.025 mol of BaCO₃ was added and the mixture was stirred for 2 h at 50 °C until it became transparent. The colorless clear solution thus obtained was heated at 130 ± 5 °C to promote polymerization and remove excess solvents. On continued heating at ~130 °C over several hours, the solution be-

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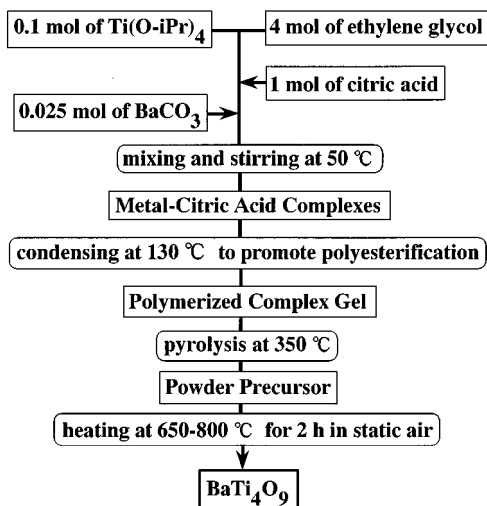


FIG. 1. Flow chart for preparing BaTi_4O_9 by the polymerized complex method.

came highly viscous with a change in color from colorless to deep yellow, and finally it gelled into a transparent brown glassy resin. It is noteworthy that no visible formation of precipitation or turbidity was observed during the polymerization and gelation. Charring the resin at 350°C for 2 h in an electric furnace resulted in a black powder, which is hereafter referred to as a ‘‘precursor.’’ The precursor was heat treated at $650\text{--}800^\circ\text{C}$ for 2 h in static air on an Al_2O_3 boat followed by natural furnace cooling to room temperature. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out to follow the decomposition of precursors with a heating rate of $10^\circ\text{C}/\text{min}$. For the purpose of comparison, BaTi_4O_9 was also prepared by the conventional solid state reaction at 900°C for 20 h using an intimate mixture of BaCO_3 and TiO_2 achieved by mechanical grinding for 2 h. The products were characterized by x-ray diffraction (XRD) using $\text{Cu } K\alpha$ radiation to identify various possible phases formed.

Both powders of BaTi_4O_9 synthesized by the PC and the solid-state reaction route were combined with a fixed amount of RuO_2 (1 wt % of Ru relative to BaTi_4O_9) in exactly the same manner as follows: (i) Powders of BaTi_4O_9 were suspended into aqueous solutions containing RuCl_3 and the suspension was stirred for 4 h at $\approx 70^\circ\text{C}$ until most of the water was evaporated. (After this procedure water was added and the solution was again evaporated to dryness.) (ii) The resulting mass was dried at 100°C for 12 h. (iii) The impregnated BaTi_4O_9 was heat treated at 500°C for 2 h under flowing H_2/N_2 gas (H_2 2% + N_2 98%), followed by oxidation at 475°C in air for 7 h. The powdered photocatalysts thus obtained were suspended into pure water. The photodecomposition of water by $\text{BaTi}_4\text{O}_9/\text{RuO}_2$ was then carried out at 60°C in a closed gas-circulation reaction vessels under irradiation of light from a high-pressure Hg lamp operated at 500 W. H_2/O_2 gases evolved were analyzed by a gas chromatograph. The specific surface area of the samples was measured by the conventional three-point BET method using nitrogen gas as absorbent.

Figure 2 shows typical TG-DTA curves of a Ba–Ti pre-

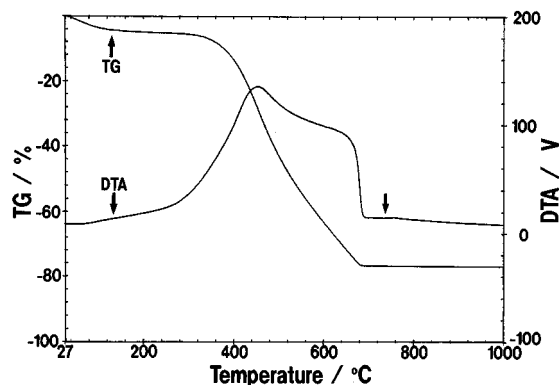


FIG. 2. TG-DTA curves of the Ba/Ti=1/4 composition precursor.

cursor fired in air. The TG curve shows a continuously small weight loss up to $\approx 320^\circ\text{C}$ and another larger weight loss extending up to $\approx 680^\circ\text{C}$. The first weight loss is mostly due to dehydration and evaporation of volatile organic components. The second large weight loss between 320 and 680°C can be ascribed to decomposition of organics involved in the precursor. The DTA scan of the precursor at a heating rate of $10^\circ\text{C}/\text{min}$ in static air shows a large exotherm feature corresponding to the large weight loss observed by TG between 320 and 680°C , which can be attributed to burnout of most of organics involved in the precursor. A relatively weak exotherm feature starting at $\approx 730^\circ\text{C}$ (marked with an arrow) in the DTA curve can probably be attributed to the onset of crystallization into BaTi_4O_9 according to the XRD data (Fig. 3).

The XRD patterns of powders obtained after calcining the precursor in air at three different temperatures for 2 h are depicted in Fig. 3 in 2θ range of $10^\circ\text{--}55^\circ$. The precursor heat treated up to 650°C was primarily amorphous in structure, as shown by the broad continuum in the XRD in Fig. 3(a). Drastic crystallization has occurred during the heat treatment of the precursor in air at 700°C for 2 h. All the XRD patterns of the powders heat treated above 700°C ex-

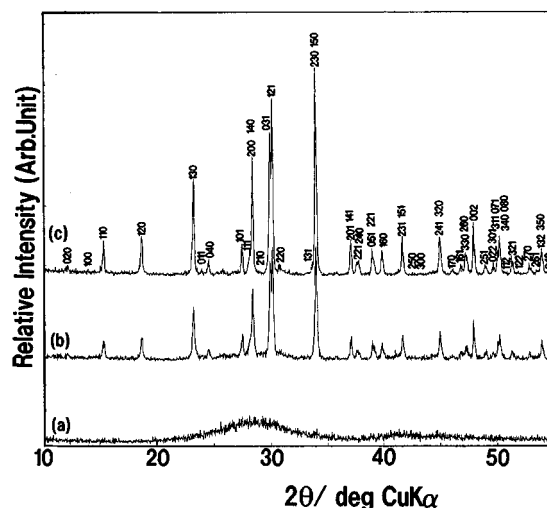


FIG. 3. X-ray diffraction patterns of products obtained by heating the Ba/Ti=1/4 composition precursor in static air for 2 h at 650°C (a), 700°C (b), and 800°C (c).

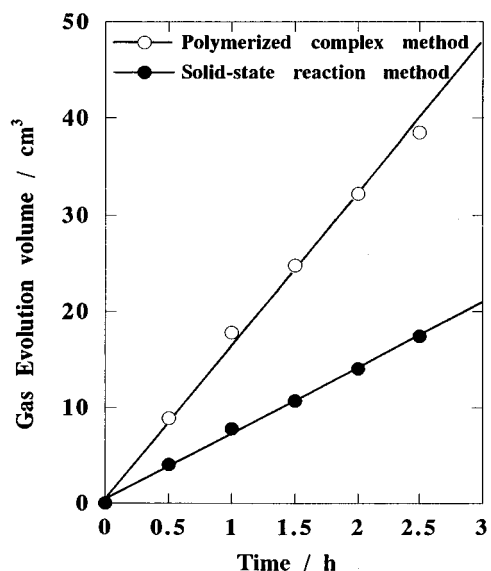


FIG. 4. Photoassisted water decomposition on RuO₂-impregnated BaTi₄O₉. The BaTi₄O₉ powders were prepared by polymerized complex method (○) or solid state reaction method (●). The amount of RuO₂ is the same for both the BaTi₄O₉ powders (1 wt % or Ru relative to BaTi₄O₉).

hibited a pure orthorhombic phase of BaTi₄O₉ in good agreement with the diffraction pattern observed for this compound by Phule *et al.*¹⁴ It should be stressed here that the impurity phases BaTi₅O₁₁, Ba₄Ti₁₃O₃₀, and BaTi₂O₅, which are most frequently formed as by-products during the synthesis of BaTi₄O₉, were not detected by XRD. The temperature (700 °C) at which pure BaTi₄O₉ forms *via* the PC method is so far the lowest processing temperature for this compound.

Figure 4 shows total gas (H₂+O₂) evolution volumes with illumination time and compares the photocatalytic activity of the BaTi₄O₉/RuO₂ sample prepared at 700 °C by the PC route with that of another sample prepared at 900 °C by the conventional solid-state reaction method. Note that the total amount of RuO₂ in each powder is exactly the same as mentioned before. On the assumption that H₂O is stoichiometrically decomposed into H₂ and (1/2)O₂, the maximum rates of photoassisted evolution of H₂ and O₂ were estimated from Fig. 4 to be 420 and 210 μmol h⁻¹

g⁻¹, respectively. It is quite obvious that the BaTi₄O₉/RuO₂ sample *via* the PC route has shown 2.4 times higher photocatalytic activities compared to those for the sample prepared by the solid-state reaction method. The remarkable acceleration of the photocatalytic reaction is at least partly attributable to the fact that the BaTi₄O₉/RuO₂ powder *via* the PC route has a considerably large surface area (~30 m²/g) when compared with ~5 m²/g for the solid-state reaction powder. These results would indicate that the PC route is a promising methodology for preparing the host BaTi₄O₉ compound with a large surface area that increases the RuO₂ deposition sites developed on the surface of BaTi₄O₉, thus substantially improving the photocatalytic activity of BaTi₄O₉/RuO₂. It should, however, be noticed that the photocatalytic process can be influenced not only by the particle size of BaTi₄O₉ but also by how evenly the RuO₂ is distributed over the surface of BaTi₄O₉. To clarify the latter issue, transmission electron microscopic analysis is ongoing.

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