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Synthesis of RuO_2-loaded $BaTi_nO_{2n+1}$ ($n = 1$, 2 and 5) using a polymerizable complex method and its photocatalytic activity for the decomposition of water

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A polymerizable complex (PC) technique was utilized to prepare fine powders of high purity $BaTi_nO_{2n+1}$ with $n = 1$, 2 and 5 at lower temperatures than those used for the ordinary solid-state reaction procedure. The formation of pure $BaTi_nO_{2n+1}$ occurred when precursors obtained from PC-derived gel materials were heat-treated at 800–900 °C in static air for 2 h. $BaTi_nO_{2n+1}$ powders were subsequently converted to RuO_2-loaded materials, and their photocatalytic activities for the decomposition of water were examined. While the RuO_2–$BaTi_2O_5$ ($n = 2$) and RuO_2–$BaTi_5O_{11}$ ($n = 5$) materials exhibited photocatalytic activity for water decomposition into H_2 and O_2 in approximately stoichiometric amounts ($H_2 : O_2 = 2 : 1$) under UV light irradiation with specific hydrogen gas evolution rates of 125 and 52 μmol h^{-1} g^{-1}, respectively, the RuO_2–$BaTiO_3$($n = 1$) exhibited a very low activity of less than 1 μmol h^{-1} g^{-1}. The lack of a significant occurrence of photocatalysis in $BaTiO_3$ was explained in terms of its crystal structure possessing only a very small polyhedral distortion.

Introduction

Some of compounds in the BaO–TiO_2 system are of importance in materials science because of their attractive ferroelectric and dielectric properties, and in particular compounds with a TiO_2-rich region such as $BaTi_4O_9$, $Ba_2Ti_9O_{20}$ and $BaTi_5O_{11}$ have found potential applications as microwave dielectric resonator filters.[1–5] Among them, $BaTi_4O_9$ combined with RuO_2 has recently emerged as a new photocatalyst for stoichiometrically complete photodecomposition of water under UV light irradiation.[6-8] It is therefore interesting to test whether certain barium titanate compounds other than $BaTi_4O_9$ show such photocatalytic properties. The compounds chosen for this study include $BaTiO_3$, $BaTi_2O_5$ and $BaTi_5O_{11}$.

The standard method of preparing known compounds in the BaO–TiO_2 system is the so-called solid-state reaction route, which involves mixing mechanically $BaCO_3$ and TiO_2 followed by repeated cycles of grinding and firing at high temperatures (1100–1300 °C) for the completion of the solid-state reaction.[1,2,9,10] A method based upon heat-treatment at high temperatures is not suitable for catalytic applications of oxide ceramics, since the catalytic activity is generally decreased with an increase in the synthetic temperature as a consequence of large grain growth owing to the high-temperature heat treatments. Thus the preparation of the catalyst at a lower temperature produces a material which possesses a higher activity intrinsically, probably by virtue of a greater specific surface area.

The main goal of this paper is therefore twofold: on the one hand it is aimed at demonstrating the feasibility of a polymerizable complex (PC) route,[11–15] known originally as the Pechini route,[16] for the synthesis of barium titanates at a lower temperature than that used in the ordinary solid-state reaction procedure, and on the other hand to report on the newly identified photocatalytic activities for the stoichiometric decomposition of water in RuO_2–$BaTi_2O_5$ and RuO_2–$BaTi_5O_{11}$ materials.

Experimental

Preparation of host $BaTi_nO_{2n+1}$ ($n = 1$, 2 and 5)

Our previous studies have indicated that the Pechini-type PC method is quite capable of producing photocatalysts with larger activities for the decomposition of water compared to those for samples prepared by the traditional solid-state reaction method at high temperatures.[17–20] Powders of $BaTi_nO_{2n+1}$ with $n = 1$, 2 and 5 were synthesized by this PC method, as outlined in Fig. 1.

Titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$, abbreviated as $Ti(O\text{-}iPr)_4$) and barium carbonate ($BaCO_3$) were used as starting chemicals. After dissolving $Ti(O\text{-}iPr)_4$ into ethylene glycol ($C_6H_6O_2$, abbreviated as EG), anhydrous citric acid ($C_6H_8O_7$, abbreviated as CA) with Ti : CA = 1 : 10 was dissolved, followed by the addition of $BaCO_3$. The mixture was magnetically stirred for 1 h at 50 °C to produce a transparent solution. The solution thus prepared was heated at 130 °C for several hours to promote polymerization and to obtain a polymeric gel. The gel was pyrolyzed at 350 °C to form a powder precursor for $BaTi_nO_{2n+1}$, which was subsequently heat-treated in a furnace in air for 2 h at 800 °C for $n = 1$ and 5 and at 900 °C for $n = 2$.

Preparation of RuO_2-loaded $BaTi_nO_{2n+1}$ ($n = 1$, 2 and 5)

Powders of $BaTi_nO_{2n+1}$ were suspended in aqueous solutions containing $RuCl_3$(1 wt% of Ru relative to the host barium titanate), and the water was evaporated at 70 °C for several hours. The residue was then dried at 100 °C for 12 h. The Ru-impregnated $BaTi_nO_{2n+1}$ was heat-treated at 500 °C for

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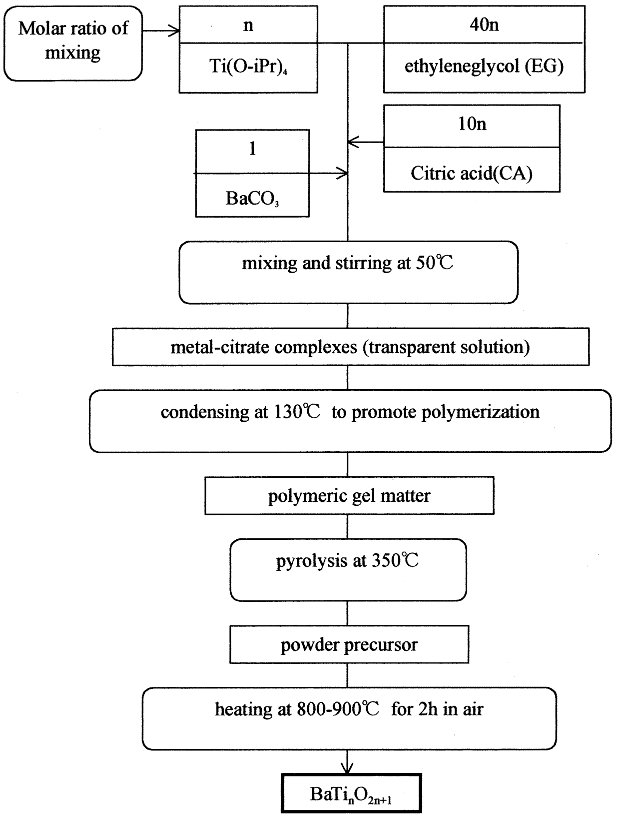

Fig. 1 Flowchart for the polymerizable complex (PC) procedures used to prepare $BaTi_nO_{2n+1}$ powders.

2 h under flowing H_2–N_2 gas(H_2 2% + N_2 98%), followed by oxidation at 475 °C under flowing air for 7 h.

Characterization

The products were characterized by X-ray diffraction (XRD) using CuKα radiation (Model MXP^{3VA}, Mac Science) and Raman scattering with excitation using the 514.5 nm line of an Ar laser (Jobin Yvon T64000) for phase identification. Ultraviolet-visible (UV-Vis) diffuse reflectance spectra were measured for the products using a Shimadzu UV-2400PC spectrometer to evaluate their absorption edges and thereby band gap energies. An inductive-coupled-plasma (ICP) analysis was carried out for the final $BaTi_nO_{2n+1}$ products in order to confirm their stoichiometries; Values of 0.99 ± 0.02, 2.00 ± 0.03 and 5.00 ± 0.05 were obtained for $n = 1$, 2 and 5, respectively.

The photodecomposition of water by RuO_2–$BaTi_nO_{2n+1}$ was carried out in an inner irradiation reaction cell made of quartz, which was connected with a gas-closed circulation system. The experimental setup is basically similar to what was reported by Kudo's group.[21] The powdered photocatalyst (0.5 g of each) was suspended by stirring in 600 ml of distilled water and irradiated using a high-pressure Hg lamp operated at 100 W. The H_2–O_2 gases evolved were analyzed at hourly intervals for a total reaction time of 4–5 h.

Results and discussion

Phase purity of $BaTi_nO_{2n+1}$ ($n = 1$, 2 and 5)

The XRD patterns of powders obtained after calcining each individual powder precursor for $BaTi_nO_{2n+1}$ ($n = 1$, 2 and 5) are shown in Fig. 2(a)–(c) in a 2θ range of 20°–70°. All the well-defined peaks in the XRD patterns of Fig. 2(a)–(c) exhibited pure phases of $BaTiO_3$ ($n = 1$), $BaTi_2O_5$ ($n = 2$) and $BaTi_5O_{11}$ ($n = 5$), respectively, in good agreement with diffraction patterns simulated by Rietvelt analyses using their respective known crystal structures.[22–25] An important aspect that it is worthwhile to mention is that no reflections from $BaCO_3$ and TiO_2 were observed as distinct impurities. The Raman spectra of our $BaTi_nO_{2n+1}$ samples also show no evidence for the presence of $BaCO_3$ as shown by the complete absence of the strongest Raman peak at 1059 cm^{-1} characteristic of $BaCO_3$ as shown in Fig. 3. It is the Raman spectroscopy that is capable of detecting impurities consisting of very small crystallites not easily identified with the XRD technique because of their diffuse reflections.[26,27] No detection of $BaCO_3$ and TiO_2 from all the Ba : Ti = 1 : n composition precursors would be considered as an implication of improved mixing of the constituent barium and titanium ions in the respective powder precursors.

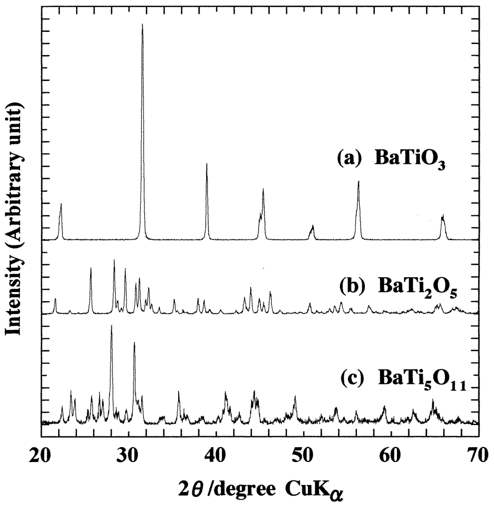

Fig. 2 X-Ray diffraction patterns of $BaTiO_3$ (a), $BaTi_2O_5$ (b) and $BaTi_5O_{11}$ (c) synthesized by the PC method.

One of the common problems in the synthesis of barium titanates by sol–gel routes is the difficulty in controlling the rapid hydrolysis of Ti-alkoxides (chemicals most often used as sources of Ti in sol–gel processes) compared with barium species. Different hydrolysis and condensation rates for the precursors often lead to premature precipitation of insoluble titanium oxo species or result in localized enrichment of titanium species.[28] The previously reported sol–gel synthesis of $BaTi_4O_9$ is a case in point.[29] Gels derived from Ba and Ti alkoxide precursors have produced strongly multiphase

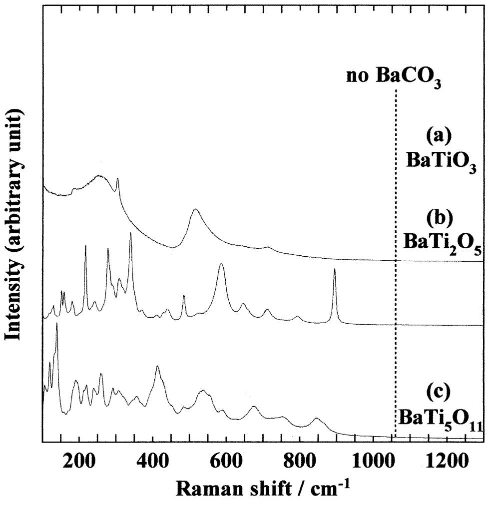

Fig. 3 Raman spectra of $BaTiO_3$ (a), $BaTi_2O_5$ (b) and $BaTi_5O_{11}$ (c) synthesized by the PC method. The position of the strongest Raman peak at 1059 cm^{-1} characteristic of $BaCO_3$ is indicated by the dotted line.

samples even after heat-treatment at 1200 °C. The preferential hydrolysis of Ti-alkoxides can form Ti-rich clusters, which destroys the cation composition of the original solution. This tells us that Ti-alkoxides should be modified by certain chelating ligands such as acetic acid[30] and acetylacetone[31] to control their reactivity by occupying active sites for hydrolysis around the Ti center.

Our success in preparing pure $BaTi_nO_{2n+1}$ at 800–900 °C arises from the characteristics of the PC method used for the synthesis. The PC method is based on the polymerization between citric acid (CA) and ethylene glycol (EG) in the presence of the required amounts of soluble metal salts to form a polyester-type gel matter, inside which metal–CA complex species remain soluble to sustain the scale of mixing of different metals almost molecularly homogeneous.[32–37] In the case of $BaTi_nO_{2n+1}$, the individual Ba– and Ti–CA complexes can be immobilized in a rigid polyester network while preserving the initial stoichiometric ratio of Ba and Ti upon polymerization. Immobilization of the metal complexes in a rigid polymer would largely reduce the marked tendency for Ti-species to be preferentially hydrolyzed, which might occur in the alkoxide-based sol–gel technique. This remarkable characteristic of the PC route allows us to synthesize $BaTi_nO_{2n+1}$ at a lower temperature than that used for the ordinary solid-state reaction procedure without passing through the formation of other barium titanates with Ba : Ti ratios at deviance from each individual desired Ba : Ti = 1 : *n* stoichiometry.

Photocatalytic activities of RuO_2–$BaTi_nO_{2n+1}$ for water decomposition

Fig. 4 shows the time courses of H_2 and O_2 evolution over the RuO_2–$BaTi_2O_5$and RuO_2–$BaTi_5O_{11}$ photocatalysts prepared by the PC method at 900 °C for 2 h and at 800 °C for 2 h, respectively. For comparison, H_2 gas evolution volumes with irradiation time for the RuO_2–$BaTiO_3$sample are also plotted in Fig. 4. The RuO_2–$BaTi_2O_5$and RuO_2–$BaTi_5O_{11}$photocatalysts give H_2 and O_2 steadily in approximately stoichiometric amounts (*i.e.* $H_2 : O_2 = 2 : 1$) from pure water under UV light irradiation with specific H_2 evolution rates of 125 and 52 μmol h^{-1} g^{-1}, respectively. It is worth mentioning here that there is an essential question as to the origin of the oxygen released during the irradiation process; *i.e.* it is not absolutely clear if the oxygen originates solely from the water, since for in instances it could also originate from the lattice oxygen of the solid compounds themselves. It would be the latter case when a given compound readily forms nonstoichiometric compositions, which may cause a photo-induced corrosion of the lattice possibly releasing oxygen in an irregular way. On the contrary, compounds in the BaO–TiO_2 system are known to form highly stoichiometric compositions,[1–5] meaning that the photo-induced corrosion of the lattice is hard to occur. No appreciable change of XRD patterns of our photocatalysts before and after the irradiation may also support our proposition that there was no significant photo-corrosion during the irradiation process. Moreover, the fact that the oxygen is steadily released with irradiation time may indicate that the oxygen originates from the water. This is because if any defects are produced by the photo-corrosion of the lattice, they can act as inactivation centers, giving rise to severe deterioration of the photocatalytic activities. In contrast to the case for $BaTi_2O_5$ and $BaTi_5O_{11}$, the RuO_2–$BaTiO_3$sample shows only a little activity with a specific H_2 evolution rate less than 1 μmol h^{-1} g^{-1}, and no O_2 gas evolution was observed from the system.

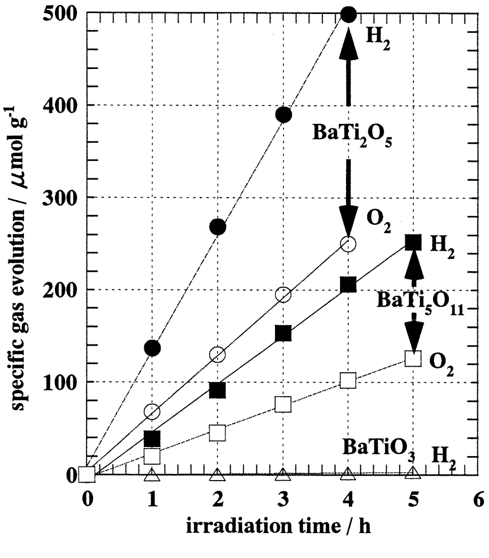

Fig. 4 Time course of specific gas evolution over the RuO_2–$BaTi_2O_5$ (●, H_2; ○, O_2), RuO_2–$BaTi_5O_{11}$ (■, H_2; □, O_2) and RuO_2–$BaTiO_3$ samples (△, H_2).

Although the factors affecting photocatalytic activities of the barium titanate systems tested in this study are too widespread to be understood unequivocally, at least the purity, band gap, surface area and crystal structure can be examined to gain further insight into different photocatalytic activities among various barium titanate materials. In Table 1 are shown for various barium titanates their individual synthetic temperatures, photocatalytic activities with respect to H_2 evolution rates, band gaps determined from UV-Vis reflectance spectra, specific surface areas determined from the conventional three-points Brunauer–Emmett–Teller (BET) method using nitrogen gas as absorbent and polyhedral distortion around Ti centers (Δ) using published crystallographic data[22–25,38] defined as:[39]

$$\Delta = 1/N\Sigma[(\gamma_i - \gamma_m)/\gamma_m]^2$$

with $N = 6$ for octahedral distortion, where γ_i is an individual Ti–oxygen distance and γ_m is a mean Ti–oxygen distance in an octahedron. Of the systems listed in Table 1, all contain a TiO_6 octahedron.

First, it can be seen from Table 1 that the specific surface area does not account for the difference in photocatalytic activities among different barium titanate systems. For well-crystalline materials practically free from any defects, the photocatalytic activity of the same compound is thought to be primarily governed by their surface area.[18,40,41] All the samples

Table 1 Selected factors possibly affecting the photocatalytic activities for water decomposition in various kinds of barium titanate systems

					Polyhedral distortion, $10^4\Delta^d$					
System	Synthesis temperature/°C	H_2 evolution rate/μmol h^{-1} g^{-1}	Band gap^c/eV	Specific surface area/m^2 g^{-1}	Ti(1)	Ti(2)	Ti(3)	Ti(4)	Ti(5)	Mean
RuO_2–$BaTiO_3$	800	~0.5	3.7	22	~0	—	—	—	—	0
RuO_2–$BaTi_2O_5$	900	125	3.7	10	126.5	40.2	10.3	—	—	59.0
RuO_2–$BaTi_4O_9$^{a}	700–1100	100–600^b	3.7	1–20^b	67.1	19.9	—	—	—	43.5
RuO_2–$BaTi_5O_{11}$	800	52	3.8	15	24.2	20.2	3.4	47.4	11.5	21.3

^{a}From ref. 18. ^{b}Depending upon the synthesis temperature. ^{c}Estimated from onset of the absorption in UV-Visible spectra. $^d\Delta = 1/N\Sigma[(\gamma_i - \gamma_m)/\gamma_m]^2$, from ref. 36. See text.

listed in Table 1 are well-crystallized as far as they have been examined by XRD. Moreover, there seems to be no correlation between band gaps and photocatalytic activities for barium titanate systems. On the contrary, the polyhedral distortion around the Ti centers, Δ, seems to be indispensable for the occurrence of photocatalysis in barium titanate materials. While the RuO_2–$BaTiO_3$ systems showing a very little photocatalytic activity have very small values of Δ, the other three host compounds ($BaTi_2O_5$, $BaTi_4O_9$ and $BaTi_5O_{11}$) showing large photocatalytic activities involve highly distorted TiO_6 octahedra, *i.e.* leading to larger Δ values.

It has been previously proposed that the dipole moment arising from the strongly distorted TiO_6 octahedra in $BaTi_4O_9$ is useful for the efficient production of photoexcited charges, leading to its high photocatalytic activity for water decomposition under UV light irradiation.[6–8] Subsequently a model explaining the photocatalytic decomposition of water in $BaTi_4O_9$ has been proposed,[42] in which O^- surface radical species, which are generated from lattice O^{2-} upon UV light irradiation,[43,44] are responsible for creating hole centers. According to this model, Ti–O bond scission is indispensable for producing the O^- surface radical species, and thereby for giving rise to the photocatalytic decomposition of water.[42] It is then plausible that the Ti–O bond scission occurs more easily at weaker bonds, *i.e.* for longer Ti–O bonds in TiO_6 octahedra.[45] In general, a larger distorted TiO_6 octahedron having a larger value of Δ exhibits a larger range of Ti–O bond distances. For instance, $BaTi_4O_9$ possesses two kinds of strongly distorted TiO_6 octahedra with Δ values of 67.1×10^{-4} and 19.9×10^{-4} for the Ti(1) and Ti(2) coordination octahedra, respectively, as shown in Table 1. For the case of $BaTi_4O_9$,[38] the $Ti(1)O_6$ octahedron is composed of 6 Ti–O bonds with distances of 1.737, 1.923, 2×1.958, 2.044 and 2.282 Å, whereas the corresponding bond distances for the $Ti(2)O_6$ octahedron are 1.855, 1.879, 2×1.941, 2.033 and 2.109 Å. Thus, photocatalytic active sites for water decomposition in RuO_2–$BaTi_4O_9$ might be at the longest Ti–O bond with a distance of 2.282 Å within the $Ti(1)O_6$ octahedron, where the Ti–O scission may take place at the highest probability.

A similar argument may be valid for $BaTi_2O_5$ and $BaTi_5O_{11}$. For instance, in the case of $BaTi_2O_5$, there is a pronounced distortion of the coordination octahedron around Ti(1) with $\Delta = 126.5 \times 10^{-4}$ (see Table 1). Ti(1) is displaced largely from the center of the octahedron towards one of the 6 oxygen atoms, forming the shortest Ti–O bond of 1.724 Å.[24] Four Ti–O distances are in the range 1.875–2.056 Å, and the last Ti–O bond is considerably longer, 2.466 Å, at which the Ti–O scission may most probably take place.[24] It should be noticed that $BaTiO_3$ with a very small polyhedral distortion ($\Delta \sim 0$) exhibited negligible photocatalytic activity (see Table 1). This may in turn indicate that a large polyhedral distortion giving rise to long Ti–O bonds in the structure would be responsible for the occurrence of photocatalysis in barium titanate materials. However, the reason for the observed difference in photocatalytic activities among $BaTi_2O_5$, $BaTi_4O_9$ and $BaTi_5O_{11}$ with large polyhedral distortions remains unclear. A further study is required to clarify this issue.

Conclusion

Pure $BaTi_nO_{2n+1}$ with $n = 1$, 2 and 5 has been successfully synthesized by heat-treating the PC powder precursors in air at reduced temperatures (800–900 °C) for 2 h. The success in lowering the preparation temperature indicates an improved level of mixing of barium and titanium ions in the powder precursors. Powders of $BaTi_2O_5$ ($n = 2$) and $BaTi_5O_{11}$ ($n = 5$) combined with RuO_2 decomposed water to hydrogen and oxygen in a stoichiometric ratio under UV light irradiation with H_2 evolution rates of 125 and 52 $\mu mol\ h^{-1}\ g^{-1}$, respectively. By contrast, virtually no photocatalytic activity was observed for RuO_2-loaded $BaTiO_3$. It is suggested that the large distortions in TiO_6 octahedra might be responsible for the occurrence of photocatalytic activities for water decomposition by RuO_2–$BaTi_nO_{2n+1}$ materials.

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