Barium titanate dispersion obtained by a high pressure methods and light resistant composites containing the nanoparticles

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To improve the light resistance of the organic–inorganic composite for optical use, barium titanate (BTO) dispersion was prepared instead of titinate (TiO2) dispersion by a high pressure reaction between titanium oxide (TiO2) dispersions treated with silane-coupling reagent and barium hydroxide [Ba(OH)2]. The obtained BTO was observed by transmission electron microscope (TEM) and its diameter was less than 10 nm. This seemed the result from the treatment of the TiO2 before the reaction. In addition, X-ray diffraction analysis (XRD) indicated TiO2 crystals didn’t remain in the BTO. Transparent composites composed of 2-hydroxy-butylacrylate as the organic matrix and the BTO or the TiO2 as the inorganic filler were prepared. The composite including the BTO showed much longer decomposition time than that of TiO2 in the light (405 nm) resistance test. This indicates that the BTO has lower photocatalytic activity than the TiO2.

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1. Introduction

Transparent inorganic–organic composite materials are very attractive for optoelectronics devices.1) Especially the composites possessing a high refractive index are applied for optical lens, light extraction layers and anti-refraction layers.1,2) Titanium oxide (TiO2, refractive index = 2.5) is generally used as a part of high refractive composite materials.3)–6) However, TiO2 should not be applied for inorganic–organic composites since TiO2 has photocatalytic activity and destroy the organic components in the composites.7) Instead of TiO2 materials, barium titanate oxides (hereafter referred to as BTO, refractive index = 2.4) can be used as a component of high refractive index composites because they have a quite low photocatalytic activity.8)

BTO nanoparticles are prepared using sol–gel methods9),10) and hydrothermal methods.11)–14) Kuwabara et al. prepared BTO nanoparticles using a Ba metal and Ti alkoxides from the high-content sol–gel method.9) However, transition metal alkoxides are very difficult to use since they are higher moisture sensitive compounds and very expensive. On the other hand, relatively large BTO particles can be prepared easily by the high pressure hydrothermal reaction between Ba(OH)2 and TiO2. The prepared BTO was too agglomerated (more than 20 nm) to apply for transparent devices.

In this study, we prepared TiO2 covered with a silane-coupling reagent as a covering material for affinity to the organic matrix of the composite before the high pressure reaction. And the reaction was carried in a heterogeneous environment (so we call this method improved high pressure method hereafter referred to as “IHM” in distinction from a traditional aqueous hydrothermal method hereafter referred to as “AHM”). As a result, the transparent dispersion of BTO (hereafter referred to as “IHM-BTO”) was obtained. The diameter of the IHM-BTO particle observed by transmission electron microscope (TEM) was less than 10 nm. At this time, we could prepare the sample for the initial objective: transparent BTO-organic composite as an optical material sample that should have high refractive index and a light resistance against 405 nm laser. Due to the process of IHM, the IHM-BTO particle already had a dispersibility in the organic matrix. So we just mixed IHM-BTO and the matrix. The obtained composite had been improved on light resistance compared with TiO2-organic composite.

2. Experimental procedure

2.1 Materials

Titania sol; SAD01-W (diameter: 5 nm, 15 wt%, specific gravity = 1.1) was obtained from Sakai Chemical Industry Co., Ltd. Barium Hydroxide Octahydrate Ba(OH)2·8H2O was obtained from Wako Pure Chemical Industries, Ltd. Silane-coupling reagent; 3,3,3-Trifluoropropyltrimethoxysilane (hereafter referred to as “FAS-3”) was obtained from Tokyo Chemical Industry Co., Ltd. Distilled water, aqueous ammonia (28%), methanol, ethanol, acetic acid and methyl isobutyl ketone (hereafter referred to as MIBK) were obtained from Junsei Chemical Co., Ltd. Aqueous ammonia (28%) was diluted by the same volume of ethanol. This solution is hereafter referred to as “NH4/EtOH”. The acrylic resin; 2-hydroxybutylacrylate for the organic matrix of the composite and the photoinitiator; 1-hydroxycyclohexylphenylketone were obtained from Tokyo Chemical Industry Co., Ltd.

2.2 Aqueous hydrothermal method (AHM)

SAD01-W was measured by a micro pipette to involve 200 mg as TiO2 particles and diluted by the distilled water up to 20 ml in
Table 1. The measured weights for traditional aqueous hydrothermal method (AHM) and the method developed in this study (IHM). No. 0; AHM, No.1 to 6; IHM

| No. | Designed composition | TiO2 (as particles) | Ba(OH)2·8H2O |
|-----|----------------------|---------------------|---------------|
| 0   | BaTiO3               | 200 mg              | 790 mg        |
| 1   | BaTiO3               | 498 mg              | 1967 mg       |
| 2   | Ba0.75TiO3           | 498 mg              | 1633 mg       |
| 3   | Ba0.5TiO3            | 498 mg              | 1475 mg       |
| 4   | Ba0.25TiO3           | 498 mg              | 1377 mg       |
| 5   | Ba0.05TiO3           | 498 mg              | 1279 mg       |
| 6   | Ba0.00TiO3           | 498 mg              | 1180 mg       |

2.3 Improved high pressure method (IHM)

2.3.1 Covering the particles

SAD01-W was measured by a micro pipette to involve 498 mg as TiO2 particles and diluted by the same volume of ethanol in sample vials. FAS-3 (273 μL, 1.437 mmol) was added to the vial and well mixed, and then it was left overnight at a room temperature.

The mixture solution in the sample vial turned white and gelled. Ethanol (10 mL) was added and mixed, and then the solution turned transparent and was evaporated twice adding further ethanol to obtain a dry powder. MBK (5 mL) was added to solve the powder. Subsequently, ethanol (2.5 mL) and NH4OH (5 mL) was added then they were mixed immediately. This solution is hereafter referred to as “TiO2-S”.

2.3.2 Re-crystallization

The method of the reaction between TiO2-S and barium hydroxide is described as follows. The weights of Ba/Ti molar ratio (hereafter referred to as “Ba/Ti”) series samples are shown in Table 1. The No. 2 in Table 1 (Ba/Ti = 0.83) is described typically. The other IHM samples in Table 1 were obtained by the same methods excluding the weights of Ba(OH)2·8H2O.

The distilled water (7.5 mL) and Ba(OH)2·8H2O (1.633 mg) were set in the reaction vial. The TiO2-S was poured into the reaction vial, followed by ethanol (5 mL) and MBK (15 mL).

The reaction was carried out by microwave, StartSynth (1000 W, 3 MPa resistant, 2.45 GHz) by Milestone General K.K. The operating program was: 2 min slope to 100°C, 10 min hold, 2 min slope to 165°C, 10 min hold and cooling (stop of the microwave) to <60°C. All heating was inducted by 380 W of the microwave.

After cooling, the content of the reaction vial and ethanol (2 mL) for washing the reaction vial were poured into new sample vial and leaved till the phases separate thoroughly. The upper MBK phase was decanted to new sample vial, dried to be a powder then solved by fresh MBK.

Purification was carried out. The sample was washed two times by 5 wt% of acetic acid aqueous solution, and then dried to be IHM-BTO.

2.4 Composites

The obtained IHM-BTO (Ba/Ti = 0.83, No. 2 of Table 1) were weighed and dissolved into 2-hydroxybutylacrylate to be 10 vol% composite (specific gravity of IHM-BTO was assumed 4.0 and that of 2-hydroxybutylacrylate was assumed 1.1). 0.5 wt% of 1-hydroxycyclohexylphenylketone was added to the composite. The composite was pressed between two quartz plates (0.5 mm thick) to obtain about 5 μm (for transparency analysis and light resistance test) and 100 μm (for refractive index analysis) thick membranes. The membranes (hereafter referred to as “IHM-BTO membrane”) were photo-cured by 100 mW/cm2 365 nm light. After the curing, one side of the quartz were peeled from 5 μm thick membrane, both side of the quartz were peeled from 100 μm thick membrane.

As the control sample, SAD01-W was treated as described in the “2.3.1 Covering the Particles” paragraph except for the weighing of FAS-3 was 180 μL to prepare TiO2-S. Then the composite membranes (hereafter referred to as “TiO2 membrane”) were prepared to be 10 vol% of TiO2 in 2-hydroxybutylacrylate as described above (specific gravity of the particle of TiO2-S was assumed 2.7).

The obtained AHM-BTO was not treated with FAS-3 to have the affinity with the organic matrix since it was obviously opaque.

2.5 Analysis

Transmission electron microscopy (TEM, JEM-1230, JOEL) observation was carried about the TiO2 as a raw material and the BTO by both AHM and IHM as a derived materials.

X-ray diffraction analysis (XRD, RINT-TTR III, Rigaku) was carried for the AHM and IHM-BTO particles. For IHM-BTO, element analyses were measured by inductively-coupled plasma (ICP, SPS3100, SII) about Ba/Ti = 1.00 and 0.83 sample (No. 1 and No. 2 of Table 1). About the No. 1, both before and after the purification samples were measured.

The transmittances of the membranes (5 μm) were measured by an absorption spectrometer (HITACHI, U-4100) for 200 to 700 nm.

The refractive index of IHM-BTO was calculated from the indices of IHM-BTO membrane (100 μm thick) and 2-hydroxybutylacrylate measured by an Abbe refractometer (ATAGO, DR-M2).

The light resistance was tested irradiating by 80 mW/mm2 of 405 nm laser (laser diode; Nichia Corporation, NDHV220APA, driver; ASAHDATA SYSTEMS CO., LTD. ALP-7033CB, beam profiler; COHERENT JAPAN, INC., Beam Master BM-3 Si, power meter; ADC CORPORATION, 8230, 82312B) in 80°C oven (Yamato Scientific Co., Ltd., DY300). The light resistance was evaluated as the attenuation of the energy transmittance from the initial.

3. Results

Figure 1 shows TEM observations of the TiO2 and the BTO particles by AHM and IHM. The diameter of the AHM-BTO particle grew to about 100 nm. On the other hand, the diameter of the IHM-BTO particle was less than 10 nm, as if it kept its primary shape.

Figure 2 shows XRD charts of AHM and IHM-BTO. The representative peak of TiO2 (2θ = 25°) was obviously observed when Ba/Ti = 0.60 and decreased as Ba/Ti increased, then almost disappeared when Ba/Ti = 0.83 that was not reaching 1.0. In addition, the charts of IHM-BTO were broader than that of AHM-BTO since the IHM-BTO particle was smaller than that of AHM-BTO (Fig. 1).

The result of the element analysis is shown in Table 2. After the purification, Ba/Ti of No. 1 sample decreased to be close to that of No. 2. Excess Ba for IHM-BTO might be outside of the membrane.
micelle consists of FAS-3 during and after the reaction.

The transmission spectrum of IHM-BTO membrane (5 μm thick) is shown in Fig. 3. IHM-BTO was considered to have a similar dispersibility and particle size distribution to the TiO$_2$ as a raw material.

The refractive index ($n_D$) of 2-hydroxybutylacrylate was 1.450 and that of IHM-BTO membrane was 1.497. Then the calculated refractive index of the IHM-BTO particle including its organic shell was 1.92.

The result of the light resistance test is shown in Fig. 4. IHM-BTO membrane had enduring period while TiO$_2$ membrane began decomposing just after the starting of the test.

4. Discussion

A unique method for synthesis of nanoparticles was found while trying to study the light resistance of composite including barium titanate (BTO) for replacement for titanate (TiO$_2$) that has photocatalytic activity. The method has two improvements compared to traditional hydrothermal method. One is that the TiO$_2$ was covered with a silane-coupling reagent as a covering material for affinity to the organic matrix of the composite before the high pressure hydrothermal reaction. The other is that the reaction was carried in the heterogeneous environment consist of organic solvent, alcohol and basic water. We called this improved high pressure method “IHM”.

Using IHM, the BTO particle was obtained without the fusion that was occurred when using AHM. We inferred the mechanism of IHM that the silane-coupling reagent (3,3,3-Trifluoropropyltrimethoxysilane, “FAS-3”) formed micelles surrounding the TiO$_2$ like a surfactant, then dissolutions and re-crystallizations were occurred in the micelles, because IHM-BTO had the excellent dispersibility (even after drying) and tolerance against
the washing by acetic acid solution. Commonly, BTO crystal is dissolved to an acid. Beforehand we found that during milling the bulk BTO to obtain small particles, the crystal peaks of XRD were disappeared by carbonic acid from the air (data not shown) and this was the opportunity to try IHM.

The reason for choosing FAS-3 as a silane-coupling reagent is affinity to fluorine containing organic matrix we were using at the beginning. Fortunately, FAS-3 was well worked as a surfactant and as a shell of the derived BTO particle to have repellence and hydrophobicity. It is expected to be highly interesting to examine various silane-coupling reagents or surfactants with IHM.

FAS-3 was highly expected to be on the surface of the derived IHM particle according to the circumstantial evidence that the IHM-BTO has enough hydrophobicity and dispersibility even after the washing. At the ICP analysis in this report, we had to dissolve IHM-BTO in hydrofluoric acid to decompose into barium and titanium. To obtain the direct evidence of the existence of fluorine, desirably -CF3 that is the characteristic functional group included in FAS-3, we are investigating trying to analyze IHM-BTO by Electron Spectroscopy for Chemical Analysis (ESCA). We may be able to report on the prospective publishing.

The microwave (MW) irradiation as the heating measure might be also the fortunate. We used MW for rapid experiments but also MW irradiation is ideal for homogeneous generation of growth of particles because MW heats the solutions uniformly.16) We are conjecturing the formation scheme of IHM-BTO as indicated in Fig. 5. According to Fig. 5, each IHM-BTO formation phase (solving, melting and separating) require the suitable temperature and reaction time respectively. Assuming that, the simultaneous heating by MW irradiation might be a good condition for IHM-BTO formation. And when examine IHM using autoclave, it may

Table 2. The result of the element analysis of IHM-BTO. Atomic weights were used 47.87, 137.33 and 16.00 for Ti, Ba and O respectively. After purification, the Ba/Ti of No. 1 sample decreased to close to No. 2. Excess Ba might be outside of the micelle consists of FAS-3 after the reaction. The total atomic content (Ti, Ba and O) is smaller than 100% because IHM-BTO includes FAS-3 and its derivatives.

| Sample No. (correspond to Table 1) | Prepared composition | Content (wt%) | Ba/Ti (molar ratio) |
|-----------------------------------|----------------------|--------------|-------------------|
| No. 1 (before purification)       | BaTiO3               | 46.1 15.1 15.1 | 1.064             |
| No. 1 (after purification)        | BaTiO3               | 45.9 18.3 18.3 | 0.874             |
| No. 2                              | Ba2TiO3              | 42.3 16.9 16.9 | 0.872             |

*1: calculated from Ti wt %. *2: molar ratio.

Fig. 3. The transmission spectrum of the 5μm thick composite membrane containing 10 vol % of IHM-BTO in 2-hydroxybutylacrylate on the quartz substrate. The transparency at the visible range indicates the high dispersibility of the particles.
require long reaction time or imperfect IHM-BTO particle may be obtained.

Barium is a member of ionic atoms while titanium is a member of the classification of glass forming. According to this, barium has weak binding to the silanol functional group compared to Titanium. So the titanium might arranged the inside of the micelle (silanol side of FAS-3) preferentially than the barium during the re-crystallization, then after the reaction, the BTO crystal core that its surface ends with Ti-O groups might be formed. The excess barium and FAS-3 derivatives might be outside the micelle and washed away by the acetic acid solution.

If the mechanism of IHM reaction is like described above, the TiO\textsubscript{2} crystal will disappear even if the barium is fewer than the titanium when the particle is small sufficiently. Assuming the size of the IHM-BTO particle obtained in this study is 6.2 nm [calculated as \(5 \times 0.5 \times 15/3 = 80 \times 0.5 \times 6/3\) nm, using the diameter of SAD01-W; 5 nm and molecular weights and specific gravities of BaTiO\textsubscript{3} and TiO\textsubscript{2}], and the lattice constant of the crystal is 0.4 nm, there will be only fifteen and a half lattices on the diameter line. This lacking barium atoms on both end of the line affects the composition of the crystal not negligibly. Limited to the IHM particles, the composition can be formalized;

\[
\text{Ba} / \text{Ti} = \frac{r^3 + (r - d)^3}{2 \cdot r^3},
\]

where \(r\) means radius of the particle, \(d\) means lattice constant and \(Ba\) means barium or other divalent ions (they also worked like barium on IHM. data not shown.). According to this equation, \(Ba/Ti\) will be lower than 1 significantly when the diameter (2\(r\)) is lower than 80 nm and \(Ba/Ti = 0.83\) when the diameter is 6.2 nm.

The calculated refractive index (\(n^D\)) of IHM-BTO was 1.92. Assuming the refractive index (\(n^D\)) of BTO core was 2.4 and that of FAS-3 derivatives shell was 1.4, the shell was expected to occupy almost half volume (48 vol\%) of IHM-BTO. This estimation can be roughly verified as follows. One is that assuming the height (van der Waals radius) of O-Si-(CH\textsubscript{2})\textsubscript{6}-CF\textsubscript{3} fragment of FAS-3 standing on the core is 0.7 nm, and the diameter of the BTO core is 6.2 nm (only inorganic can be seen in TEM), the former occupies about 46 vol\%. And the other is that in Table 2, total inorganic content (Ba + Ti + O) was around 80 wt\%, then remaining content was considered to be the organic shell. Assuming the specific gravity of the shell is 1.6 (because including silicon and fluorine), its volume should be about the same as that of the core.

If the composition of IHM-BTO was as described above, the structure of the obtained particle is probably shone in Fig. 6.

As a result, exceedingly dispersing BTO particle was obtained and the transparent organic–inorganic composite (IHM-BTO membrane) could be prepared for the light resistance test. The result of IHM-BTO membrane was qualitatively improved than that of TiO\textsubscript{2} membrane, not only on the degree of the attenuation of the energy transmittance, but also on having certain enduring period while the TiO\textsubscript{2} membrane began decomposing just after the starting of the test. Therefore, it could be considered that IHM-BTO does not have photocatalytic activity. BTO is an alternative to TiO\textsubscript{2} for organic–inorganic composite that have high refractive index and light resistance.

5. Conclusions

Barium titanate (BTO) dispersion was synthesized and the transparent organic–inorganic composite membrane including the BTO (BTO membrane) was prepared for examining light resistance comparing to the membrane including TiO\textsubscript{2}. The BTO membrane endured certain period and was inferred to have not a photocatalytic activity but other decomposing mechanism caused by 405 nm laser. BTO is a candidate for high refractive index composite such as optical materials.

To obtain the BTO dispersion, a unique high pressure reaction method had been developed between titanium oxide (TiO\textsubscript{2}) covered with a silane-coupling reagent as a covering material for affinity to the organic matrix of the composite and barium hydroxide [Ba(OH)\textsubscript{2}] in a heterogeneous environment. The obtained BTO particle was smaller than 10 nm and well dispersed.

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