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Overall water splitting by sonophotocatalytic reaction: the role of powdered photocatalyst and an attempt to decompose water using a visible-light sensitive photocatalyst

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Abstract

The role of a photocatalyst in the sonophotocatalytic reaction of water was investigated using TiO_2 photocatalysts. Based on this investigation, sonophotocatalytic water splitting using visible light was attempted. $BiVO_4$ is a visible light-sensitive material and this material is one of the candidates for O_2 evolution photocatalyst. For example, O_2 is evolved from H_2O_2 solution by photocatalytic reaction under visible light irradiation. On the other hand, H_2 is produced together with H_2O_2 from water by irradiation of ultrasound. Thus, it is expected to obtain H_2 and O_2 from water when these two reaction systems are combined. Simultaneous irradiation of visible light and ultrasound was tried to perform. As the result, liquid water was decomposed to H_2 and O_2 continuously and stoichiometrically.
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1. Introduction

Overall water splitting using visible light is very attractive and fundamental reaction of solar energy conversion, such as artificial photosynthesis. Recently, the decomposition of water in liquid phase was demonstrated using sonophotocatalytic technique in the presence of TiO_2 photocatalyst under white light illumination of a Xe-lamp [1]. Sonophotocatalysis means a photocatalysis with ultrasonic irradiation. This method is the novel idea for overall liquid water splitting because liquid water is decomposed to hydrogen and oxygen stoichiometrically and continuously by a multiple effect of sonolysis and photocatalysis.

In the case of sonophotocatalysis, overall water splitting was proposed to proceed by two-step reaction as follows [1].

Step 1. Sonochemical process:

$$4H_2O \rightarrow 2H_2 + 2H_2O \quad (1)$$

Step 2. Heterogeneous photocatalytic process:

$$2H_2O_2 \rightarrow O_2 + 2H_2O_2 \quad (2)$$

If the above two-step process is valid, the photocatalytic decomposition of H_2O_2 is an important step for this system. In order to consider the role of photocatalyst in this sonophotocatalytic system, potocatalytic decomposition of H_2O_2 should be examined in spite of a downhill reaction.

When sonication is carried out, the shock waves and cavitation occur in the solution and the photocatalyst is exposed to them. For making provision against those conditions, not only high activity but also toughness should be required of photocatalyst. As a photocatalyst for the sonophotocatalytic system, so far TiO_2 has been utilized for the reasons of its stability in solution, reasonable cost, strong oxidation power, and low poisonous characteristics [1–7].

From the viewpoint of using visible light, however, TiO_2 was undesirable photocatalyst because of large band gap. If visible light-driven photocatalyst is utilized to this system, overall water splitting should be accomplished under visible light. Fortunately, H_2O_2 is decomposed by photocatalysis using a photocatalyst, which has small band gap. As visible light sensitive materials, cadmium sulfide (CdS), iron(III) oxide (Fe_2O_3), and etc. are known. In a recent paper, it was also reported that $BiVO_4$ showed photocatalytic activity for

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O_2 evolution from an aqueous silver nitrate solution under visible light [8,9]. This photocatalyst is very attractive, although it is impossible to decompose water directly. Thus these materials are candidates for an O_2 evolution photocatalyst. In other words, they were expected to be O_2 evolution photocatalysts to construct the two-step process for water decomposition using photon and ultrasonic energy.

In this paper, firstly the relationship between the product ratio for water sonophotocatalysis and specific surface area or crystal structure for TiO_2 photocatalyst is examined in order to discuss about the role of photocatalyst in the sonophotocatalysis of water. Because the photocatalysis of H_2O_2 is thought the important process for water sonophotocatalysis system, this reaction is performed although it is impossible to accumulate the photon energy. Based on these examinations, secondly, the possibility of overall water splitting by sonophotocatalysis under irradiations of visible light and ultrasound is discussed.

2. Experimental

As the powdered photocatalysts, $BiVO_4$ (monoclinic type, prepared by aqueous process [8]), CdS (Katayama Chemical, commercial reagent), Fe_2O_3 (Wako Pure Chemical Industries, commercial reagent) were used in order to utilize visible light. Commercial TiO_{2s} were also used for discussing about the photocatalytic process in sonophotocatalysis. A Pyrex glass bulb (250–300 cm^3) containing the powdered photocatalyst suspended in the reactant solution (90–120 cm^3) was used as a reactor. The glass bulb was placed in a temperature-controlled bath (EYELA NTT-1200 and ECS-0) all time. Pure water and 1 mM H_2O_2 solution (1 mmol/l) used through this study were purged with argon gas in order to expel the air before irradiations. Simultaneous irradiation was performed from one side with a 500 W Xe-lamp (Ushio UXL500D-O) and from the bottom surface with a 200 W ultrasonic generator (Kaijo TA-4021–4611, 200 kHz) under argon atmosphere at 25°C. Sharp cut filters (Toshiba Y-43, >430 nm [1] and O-53, >530 nm [2]) were inserted to the light path in order to cut off the shorter wavelength illumination. In order to discuss about the role of powdered photocatalyst, photocatalytic decomposition of H_2O_2 was also performed. The amounts of hydrogen and oxygen were determined by gas chromatography (Shimadzu GC8AIT with an attached molecular sieve 5A column and Ar carrier gas). Hydrogen peroxide in the solution was analyzed by colorimetry (JASCO V-530, 407 nm) using titanium sulfate solution (Nacalai tesque).

3. Results and discussion

3.1. Sonophotocatalysis of water using TiO_{2s}

It is known that heterogeneous photocatalytic reaction products and their production rates depend on the kind of photocatalysts. In the case of sonophotocatalytic reaction, it is supposed that products or their yields depend on the kind of photocatalysts. In fact, the dependence of the product ratio on the kind of TiO_2 was reported [2]. However, the conclusions were against a common knowledge, i.e. the finer the particles, the worse the reaction and rutile type was more active than anatase one. In order to confirm these conclusions, sonophotocatalytic reaction of water was carried out using several kinds of TiO_2 samples, which were supplied by manufactures.

Fig. 1 shows the dependence of product ratio on the specific surface area of TiO_2. About 200 mg of TiO_2 was used in all cases. It was found that the values of product ratio were independent from specific surface area although there was a little efficiency of specific surface area in Fig. 1A. It was noted that factors other than surface area must be introduce to explain the result.

As following examination, crystal structure was investigated. Although, three types of crystals are known, rutile and anatase are the major structures of TiO_2 [10]. They must be kept distinct one from another and it is widely known that photocatalytic activity of anatase is better than that of rutile. However, a large difference in product ratio from expected value was observed for anatase samples especially in early stage of reaction (Fig. 1A). The wrong value in product ratio in Fig. 1 was caused of the short amount of evolved O_2. Namely, photocatalysis of H_2O_2 did not proceed completely.

After more irradiations, product ratios were recovered for some of anatase samples (no. 2 and 4) as shown in Fig. 1B. Another anatase samples, which had small specific surface area, recorded wrong values of product ratio continuously, even after 6 h irradiations.

Meanwhile, rutile type crystal gave an acceptable product ratio. Thus, it seemed that rutile is more desirable than anatase for sonophotocatalysis of water. This result is out of common. As a rare case, it was reported that rutile was more effective than anatase on the photocatalytic dihydroxylation of naphthalene [11]. In that article, we took notice of the presence of H_2O_2. As the photocatalytic part in sonophotocatalysis of water is the decomposition of H_2O_2, this material may be the key of the reason of high activity for rutile.

One way or another, rutile rich TiO_2 is better photocatalyst for sonophotocatalytic reaction of water.

3.2. Photocatalytic degradation of H_2O_2 in water using TiO_2 photocatalyst

Photocatalytic reaction of H_2O_2 in water was examined using several kinds of TiO_2 samples in order to confirm the

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[1] Transmittance and edge of absorption are 0.5 at 430 and 400 nm, respectively.

[2] Transmittance and edge of absorption are 0.5 at 530 and 500 nm, respectively.

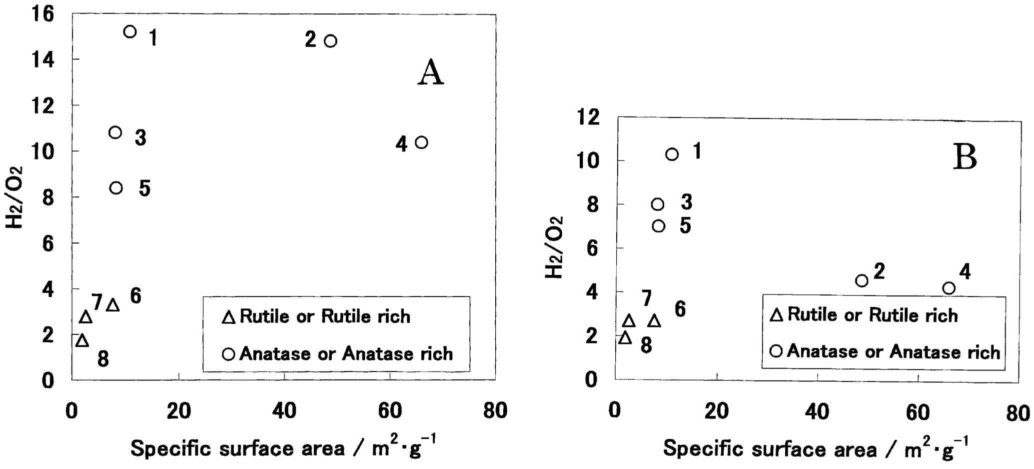

Fig. 1. Relationship between specific surface area of photocatalyst and product ratio for sonophotocatalysis of water: (A) 2 h irradiation; (B) 6 h irradiation; ultrasound, 200 kHz, 200 W; light, 500 W-Xe; atmosphere, Ar; temperature, 25°C; photocatalysts: 200 mg of commercial TiO_2 powders used were no.1 (Soekawa Chemicals, anatase and specific surface area 10.8 m^2/g), no.2 (Nippon Aerosil, P-25, anatase rich fine particle and specific surface area 48.7 m^2/g), no. 3 (Katayama Chemical, includes anatase over 90% and specific surface area 8.3 m^2/g), no. 4 (Nippon Aerosil, P-25(S6), anatase rich fine particle and specific surface area 66.0 m^2/g), no. 5 (Merck, includes anatase over 90% and specific surface area 8.3 m^2/g), no. 6 (Wako Pure Chemical Industries, includes rutile over 90% and specific surface area 7.6 m^2/g), no. 7 (Soekawa Chemicals, includes rutile over 90% and specific surface area 2.6 m^2/g) and no. 8 (Soekawa Chemicals, includes rutile over 90% and specific surface area 1.9 m^2/g).

relationship between the behavior of O_2 evolution for water sonophotocatalysis and the photocatalysis of H_2O_2.

Figs. 2 and 3 show the behavior of H_2O_2 photocatalysis. In the case of rutile rich TiO_2 (Soekawa Chemicals, tentatively named Skw-R and surface area 1.9 m^2/g), which was no. 8 in Fig. 1, H_2O_2 in the solution was reduced obviously as shown in Fig. 2. And, off course, oxygen was produced stoichiometrically. Another rutile samples also showed the similar results. Thus, it was confirmed that a rutile sample was suitable photocatalyst for the decomposition of H_2O_2.

Fig. 3 shows photocatalysis of H_2O_2 using two anatase samples, i.e. one is supplied from Soekawa Chemicals (tentatively named Skw-A, anatase and specific surface area 10.8 m^2/g) and the other is P-25 (Nippon Aerosil, anatase rich fine particle and specific surface area 48.7 m^2/g), which is popularly used. They are no. 1 and 2, respectively in Fig. 1. According to Fig. 1, both samples recorded wrong values in product ratio. In the case of Skw-A, only a little of H_2O_2 was decomposed to O_2. Some of anatase samples with small specific surface area (Katayama Chemical, includes anatase over 90% and specific surface area 8.3 m^2/g and Merck, includes anatase over 90% and specific surface area 8.3 m^2/g), which were nos. 3 and 5 in Fig. 1, respectively, indicated the similar behavior.

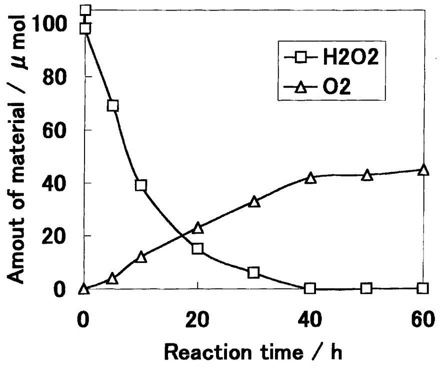

Fig. 2. Photocatalytic reaction of H_2O_2 using rutile rich TiO_2 photocatalyst; light, 500 W-Xe; atmosphere, Ar; temperature, 15°C; photocatalysts: rutile rich TiO_2 (Skw-R, Soekawa Chemicals and specific surface area 1.9 m^2/g, no. 8 in Fig. 1).

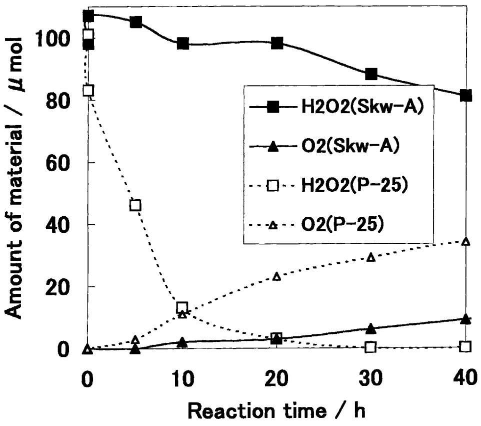

Fig. 3. Photocatalytic reactions of H_2O_2 using anatase rich TiO_2 photocatalysts; light, 500 W-Xe; atmosphere, Ar; temperature, 15°C; photocatalysts: anatase type TiO_2 (Skw-A, Soekawa Chemicals and specific surface area 10.8 m^2/g and P-25, Nippon Aerosil, anatase rich fine particle and specific surface area 48.7 m^2/g, which are nos. 1 and 2 in Fig. 1, respectively).

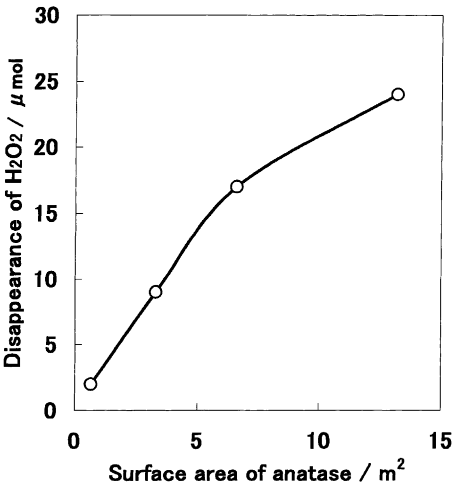

Fig. 4. Surface area dependence of amount of adsorbed H_2O_2 on TiO_2 photocatalyst before irradiation; atmosphere, Ar; temperature, 15°C; TiO_2: Nippon Aerosil, P-25(S6), anatase rich fine particle and specific surface area 66.0 m^2/g).

In the case of P-25, however, H_2O_2 decreased and O_2 was evolved. Sample of P-25 (S6) (Nippon Aerosil, anatase rich fine particle and specific surface area 66.0 m^2/g) which was no. 4 in Fig. 1, was as active as P-25. Product ratios of these active anatase were recovered after an induction period as shown in Fig. 1B. From results of Figs. 1–3, it was found that the active photocatalyst for the decomposition of H_2O_2 was suitable for the sonophotocatalysis of water.

In the cases of P-25 and P-25 (S6), why was large difference in product ratio recognized in early stage of reaction (Fig. 1A)? An important suggestion in order to answer the question was found in Fig. 3. It was observed that the concentration of H_2O_2 decreased even without irradiation (the data point at 0 h irradiation). It was thought that adsorption on TiO_2 was caused of disappearance of H_2O_2. After complete decomposition of H_2O_2 by photocatalysis, the amount of evolved O_2 was short of expected value. As P-25 and P-25 (S6) are very fine samples, the influence of surface area is considered. The effect of surface area on the amount of disappeared H_2O_2 was shown in Fig. 4. Disappeared H_2O_2 was reduced with decreasing amount of TiO_2. Thus, in the cases of P-25 and P-25 (S6), the wrong value in product ratio might be caused of adsorption of H_2O_2 on TiO_2.

Fig. 5 shows a comparison of the behavior for H_2O_2 photocatalysis between samples P-25 (no.2) and Skw-R (no. 8), namely anatase and rutile. They were made similar surface area, 0.38 m^3, by gravity control. Disappearance of H_2O_2 was negligible on both photocatalysts and rutile recorded more rapid decomposition rate.

Therefore, it was clear that the correlation of the product ratio in sonophotocatalysis of water with the behavior of H_2O_2 photocatalysis. Consequently, it was confirmed that the photocatalysis of H_2O_2 was the photocatalytic part in sonophotocatalysis of water. The photocatalyst for decomposition of H_2O_2 plays an important role in the sonophotocatalytic water splitting system.

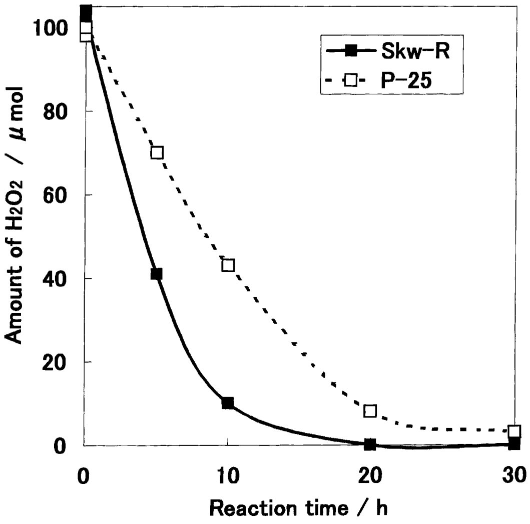

Fig. 5. Comparison of photocatalytic activities between rutile rich and anatase rich TiO_2 photocatalysts by same surface area; light, 500 W-Xe; atmosphere, Ar; temperature, 15°C; photocatalysts: 200 mg of Skw-R (Soekawa Chemicals and specific surface area 10.8 m^2/g) and 7.8 mg of P-25 (Nippon Aerosil, anatase rich fine particle and specific surface area 48.7 m^2/g).

3.3. *Oxygen evolution by photocatalysis of H_2O_2 under visible light irradiation*

Photocatalysis of H_2O_2, which was correspondent to step 2 in the sonophotocatalysis of water, was tried to perform using several kinds of visible light-sensitive materials. Table 1 shows O_2 production rates from H_2O_2 by the photocatalysis under white light irradiation of a Xe-lamp. In the case of TiO_2 photocatalyst (Skw-R), the evolution rate of O_2 was rapid. Photocatalyst of $BiVO_4$ was also effective for O_2 production. In the cases of CdS or Fe_2O_3 photocatalysts, however, O_2 was not obtained.

As shown in Fig. 6, when the sharp cut filter of Y-43 was inserted to the light path, $BiVO_4$ photocatalyst retained the reactivity although reaction rate decreased because of decreasing light flux. In the case of TiO_2 photocatalyst, on the other hand, O_2 production rate decreased vigorously. Thus, H_2O_2 could be decomposed to O_2 and H_2O using $BiVO_4$ photocatalyst under visible light (>430 nm) irradiation.

Table 1
Oxygen production rates from 1 mM H_2O_2 solution by photocatalysis using a white light illumination of a 500 W Xe-lamp

Photocatalyst	O_2 (μmol 0.5/h)
None	–
TiO_2 (Skw-R)	45
CdS	–
Fe_2O_3	–
$BiVO_4$	32

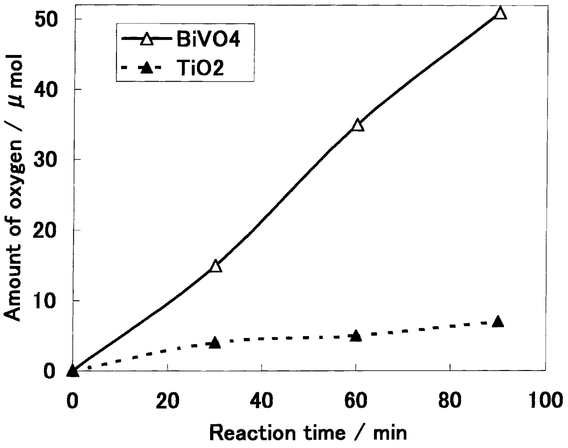

Fig. 6. Oxygen production from H_2O_2 by photocatalytic reaction under visible light irradiation (>430 nm): light, 500 W-Xe; atmosphere, Ar; temperature, 25°C.

3.4. Sonophotocatalytic decomposition of water in liquid phase under visible light irradiation

The simultaneous irradiation of ultrasound and visible light was carried out using $BiVO_4$ photocatalyst in order to decompose water by sonophotocatalysis. Fig. 7 shows the time dependencies of sonophotocatalytic reaction products from water with or without filter of Y-43. Only a little change of O_2 production rate was observed after inserting the filter. From the results of Table 1 and Fig. 6, it was supposed that O_2 production rate decreased when the cut off filter was inserted. The difference in O_2 production rate between with and without the filter of Y-43, however, was quite a small as shown in Fig. 7. In the case of photocatalysis, which was shown in former section, a desired amount of H_2O_2, such as 0.1 mmol was present in the solution. In the case of sonophotocatalysis, on the other hand, small amounts of intermediates, such as H_2O_2 were produced one after another by sonolysis and they were decomposed to O_2 quickly. It indicates that the step 1 of the reaction (Eq. (1)) is the rate-determining step for the present sonophotocatalysis of water. In addition, because of mechanical effects by ultrasonic waves, such as stirring and cleaning on photocatalyst surface, the rate of reaction might be accelerated. During the reaction, it was not confirmed to dissolve $BiVO_4$ powder in solution by ultrasonic irradiation. Thus, $BiVO_4$ was driven as a photocatalyst under visible light.

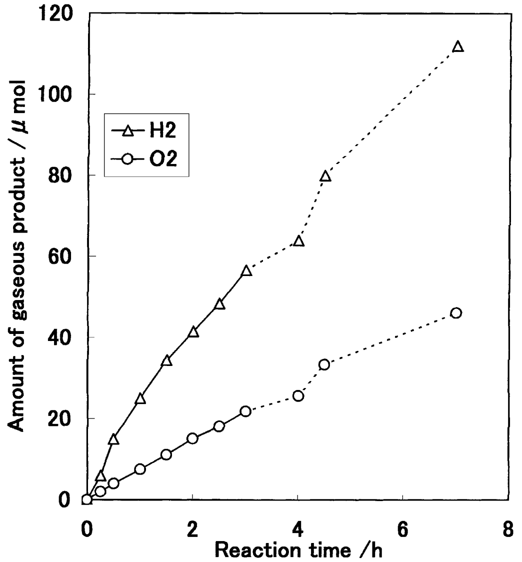

Fig. 7. Gaseous reaction products from pure water by sonophotocatalysis using $BiVO_4$ photocatalyst and its production rates before (solid line) and after (break line) inserting the shorter wavelength cutting filter: ultrasound, 200 kHz, 200 W; light, 500 W-Xe; filter, Y-43 (>430 nm); atmosphere, Ar; temperature, 25°C.

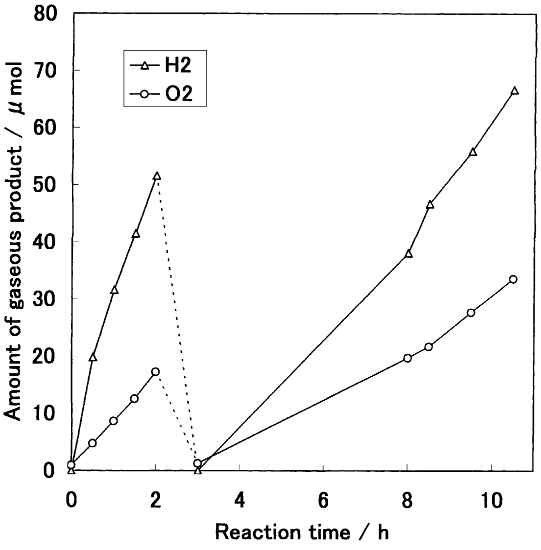

Fig. 8. Overall water splitting by repeated sonophotocatalysis using $BiVO_4$ photocatalyst under visible light and ultrasonic irradiation: ultrasound, 200 kHz, 200 W; light, 500 W-Xe; filter, Y-43 (>430 nm); atmosphere, Ar; temperature, 25°C.

Although, H_2 and O_2 could be obtained, the ratio of O_2 to H_2 was different from ideal value, i.e. 0.5 which was estimated from Eqs. (1) and (2). According to Fig. 1 or former article [1], in which TiO_2 was utilized, the wrong product ratio was sometimes obtained in early stage of reaction. In order to improve the product ratio, re-irradiation was effective after induction period. Also in the case of $BiVO_4$ photocatalyst, the improvement of products ratio was expected. The sonophotocatalysis was repeated two times as shown in Fig. 8. Although the difference in the ratio of gaseous products from ideal value was observed in the early stage of 1st run, the ratio of O_2 to H_2 came close to 0.5 for the 2nd run. Therefore, overall water splitting was accomplished under visible light (>430 nm) and ultrasonic irradiations using $BiVO_4$ photocatalyst.

When O-53 filter was inserted to the light path, only a little O_2 was evolved as shown in Fig. 9. Hydrogen peroxide, which was produced by sonolysis of water as shown

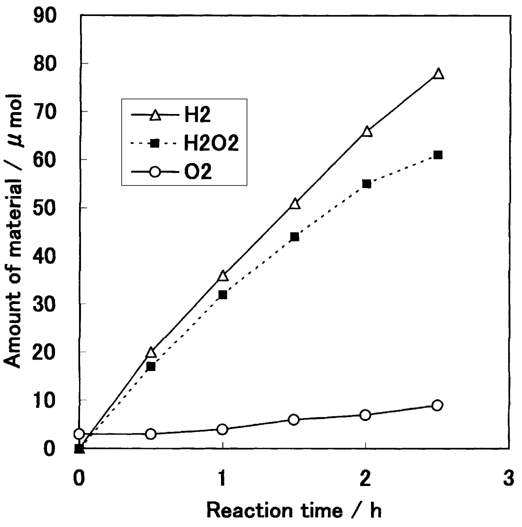

Fig. 9. Sonophotocatalytic reaction products from pure water using $BiVO_4$ photocatalyst and its production rates under visible light (>530 nm) irradiation: ultrasound, 200 kHz 200 W; light, 500 W-Xe; filter, O-53 (>530 nm); atmosphere, Ar; temperature, 25°C.

Eq. (1), remained in the solution. Thus, $BiVO_4$ was not driven as a photocatalyst under this condition. It is not thought that the photon energy, which corresponds to over 530 nm, is enough to pump up the electron from valence band to conduction band, because the band gap of $BiVO_4$ used in this experiment is 2.4 eV and the adsorption edge was 510 nm [9]. The decomposition of a little H_2O_2 together with O_2 production was also observed in Fig. 9. As a small amount of the light below 510 nm transmitted through the glass filter of O-53, quite a few number of valence band electron should be pumped up the conduction band.

4. Conclusions

In order to consider the role of photocatalyst in the sonophotocatalysis of water, photocatalysis of H_2O_2 was performed. This reaction is correspondent to photocatalytic part in the sonophotocatalysis of water. The correlation of the sonophotocatalysis of water with the photocatalysis of H_2O_2 was confirmed.

Rutile type TiO_2 with small specific surface area was suitable for the sonophotocatalysis of water.

Hydrogen peroxide could be decomposed to O_2 by photocatalysis under visible light irradiation using $BiVO_4$ photocatalyst. As H_2O_2 was the major intermediate of water sonolysis, it was expected that overall water splitting could be accomplished by the multiple effect of ultrasound and visible light. Hydrogen and oxygen were evolved continuously and stoichiometrically under simultaneous irradiation of ultrasound and visible light (>430 nm) after an induction period.

When shorter wavelength cutting filter of O-53 was inserted to the light path, reaction rate decreased vigorously. It is easy to understand this result because the band gap of $BiVO_4$ is 2.4 eV, which corresponds to 510 nm. In other words, $BiVO_4$ is driven as photocatalyst within the wavelength of the band gap energy.

Acknowledgements

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