**Effects of Pt-loading on Formation and Visible Light-Induced Photocatalytic Activity of Bismuth Titanate**

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Pt/TiO$_2$-Bi$_2$O$_3$ test catalysts were prepared by impregnating Pt on the sol-gel derived TiO$_2$-Bi$_2$O$_3$ to give these testpieces high photocatalytic activity under visible light irradiation. The optimum Pt support content and TiO$_2$ content were observed in the ranges 0.05-0.3 wt% and 17-28 wt%, respectively in the photocatalytic activity for Methylene Blue (MB) degradation on Pt/TiO$_2$-Bi$_2$O$_3$. Specifically, those 0.1Pt/17TiO$_2$-83Bi$_2$O$_3$, 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ and 0.3Pt/28TiO$_2$-72Bi$_2$O$_3$ samples showed relatively higher photocatalytic activity for the MB degradation. The results were closely related to (1) the restriction of recombination of the photo-induced electron and hole pairs by Pt, and (2) the presence of bismuth titanate with such high Ti content as built up by Pt.

Key Words

Bismuth titanate, Photocatalytic activity, Methylene Blue degradation, Pt-loading, Nucleating agent

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1. Introduction

Over the past several decades, photocatalysis using semiconductors has been extensively investigated on solar energy conversion and environmental remediation such as water and air purification, whereas it is well known that TiO$_2$ is a low-cost and nontoxic catalyst that possesses high photocatalytic activity and photostability, but is only active under UV irradiation. Therefore, it will be beneficial to develop visible-light-responsive photocatalysts for wider practical use.$^{1,2}$ Among many photocatalytic reactions, Methylene Blue (MB) is an intensely colored compound which is used in dyeing and textile printing. While it is a common water pollutant having been widely used as a model compound$^{3,4}$, the use of MB under visible light is causing controversial issues.$^{5}$

In the meantime, Bi$_2$O$_3$ shows poor photocatalytic efficiency for the decomposition of organic pollutants due to the fast recombination of the photo-induced electron-hole pairs. Accordingly, enhancement of such the photocatalytic performance of Bi$_2$O$_3$ has been attempted by extending the response range to wider wavelengths of light such as visible light or by efficiently separating the photo-induced charge carriers, along with metal doping, the loading of metal particles and the formation of hybrid semiconductor heterostructures. Bi$_2$O$_3$ is also known to have some crystalline phases such as $\alpha$-phase (monoclinic), $\beta$-phase (tetragonal), and $\gamma$-phase (cubic) as has been very lately reported on its successful application that the mixtures of $\beta$- and $\gamma$-Bi$_2$O$_3$ prepared using urea show larger specific surface areas and a higher activity for the hydrogen evolution under UV irradiation than the $\alpha$-Bi$_2$O$_3$ prepared without urea.$^{6}$

While the TiO$_2$-Bi$_2$O$_3$ system is also a candidate for the visible-light-responsive photocatalysts, the Bi$_2$O$_3$-based photocatalysts have been less reported than those TiO$_2$-based alternates. Among the Bi$_2$O$_3$-based photocatalysts,
the TiO$_2$-Bi$_2$O$_3$ homogeneous system (bismuth titanate and their heterojunction)\textsuperscript{23}~\textsuperscript{28} has attracted more attention than the TiO$_2$/Bi$_2$O$_3$ heterogeneous system\textsuperscript{29}~\textsuperscript{30}. The following bismuth titanate species are known as photocatalysts and often show higher photocatalytic activity than that of TiO$_2$ (P-25: Bi$_2$TiO$_5$ (9TiO$_2$·9Bi$_2$O$_3$ in mol%)\textsuperscript{18}~\textsuperscript{21}), Bi$_2$Ti$_4$O$_{11}$ (80TiO$_2$·20Bi$_2$O$_3$ in mol%)\textsuperscript{10}). MB degradation by bismuth titanate under visible light\textsuperscript{22}. In this case, the noble metals have a higher work function than TiO$_2$, which leads to the formation of a Schottky barrier in the TiO$_2$-metal region, preventing the electron migration from TiO$_2$ to metal. In addition, movement of the electrons located close to the Fermi level in metal is also prevented from flowing back to the conduction band of TiO$_2$. This will retard the recombination of electron-hole pairs and subsequently increase the photocatalytic activity. On the other hand, excess Pt-loading will often simultaneously attract both electrons and holes and eventually act as recombination centers\textsuperscript{23}.

As the photocatalytic activity of bismuth titanate under discussion has not yet been systematically clarified, especially in respect of visible light irradiation, along with the effects of Pt-loading on the formation and the foregoing photocatalytic activity and moreover, few reports on the MB degradation by bismuth titanate under visible light irradiation are available\textsuperscript{18}; in this reported study, Pt/TiO$_2$-Bi$_2$O$_3$ catalysts were prepared by impregnating Pt on the sol-gel derived TiO$_2$-Bi$_2$O$_3$ to give these testpieces high photocatalytic activity under visible light irradiation. Therefore, the effects of the Pt-loading on the formation of bismuth titanate and its photocatalytic activity in the MB degradation under visible light irradiation have been investigated.

2. Experimental

2.1 Preparation of Pt/TiO$_2$-Bi$_2$O$_3$ catalysts

TiO$_2$-Bi$_2$O$_3$ samples were prepared by the sol-gel method. Bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O; Nacalai Tesque, Inc., Kyoto, Japan) and titanium tetraisopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$; TTIP, Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as feedstock. 2-methoxyethanol (Nacalai Tesque, Inc., Kyoto, Japan) and 2-propanol (Nacalai Tesque, Inc., Kyoto, Japan) were used as solvents. At first, bismuth (III) nitrate pentahydrate and 2-methoxyethanol were mixed to prepare Bi$_2$O$_3$ precursor sol. Then, TiO$_2$ precursor sol (mixture of TTIP and 2-propanol) was added to this Bi$_2$O$_3$ precursor sol in the ratio of Bi$_2$O$_3$/TiO$_2$=100x (x=0-36 wt%), to which ion exchanged water was further added in the molar ratio of TTIP: H$_2$O=1:10 and stirred at 0 °C for 6 h to hydrolyze the TTIP. The resulting TiO$_2$-Bi$_2$O$_3$ gels were dried at 80 °C overnight and were calcined at 400 °C for 3 h (heating rate: 3 °C/min). Pt of y=0.05-0.3 wt% was loaded on the TiO$_2$-Bi$_2$O$_3$ samples prepared above by the impregnation method (300 °C, 3 h) using hexachloroplatinic (IV) acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O; Wako Pure Chemical Industries, Ltd., Osaka, Japan) and the ion exchanged water to enhance the photocatalytic activity. yPt/xTi-(100-x)Bi was used as abbreviation of yPt/xTiO$_2$-(100-x)Bi$_2$O$_3$ catalysts in Figures.

2.2 Characterization of catalysts

For the characterization of the Pt/TiO$_2$-Bi$_2$O$_3$ samples prepared, N$_2$ adsorption and desorption data and XRD data were obtained by Belsorp Mini II Model (MicrotracBEL Corp., Osaka, Japan), and Ultima IV Model (Rigaku, Tokyo, Japan), respectively. In the measurement, pore diameters determined by BET and BJH methods mean the average and mode for the distribution of pore diameter, respectively. UV-visible spectroscopy and photoluminescence (PL) spectroscopy were carried out by V-660 Model (JASCO Corp., Tokyo, Japan) and FP-8300ST Model (JASCO Corp., Tokyo, Japan), respectively.

The photocatalytic activity was rated by measuring the decrease in absorbance (photodegradation) of the Methylene Blue (MB) reagent (Nacalai Tesque, Inc., Kyoto, Japan) with the Pt/TiO$_2$-Bi$_2$O$_3$ samples exposed under visible irradiation; verification reaction was carried out in a reactor (quartz test tube, ID 8 mm) capped with silicone. The Pt/TiO$_2$-Bi$_2$O$_3$ samples (7.5 mg each) were placed in the reactor with MB aqueous solution (10 mg/L, 1.5 mL). The LED-lamp LED405/L-STND (Optocode Corp., Tokyo, Japan) was used as a visible light source, when the following irradiation conditions were set: wavelength range: 380-450 nm, peak wavelength: 410 nm, irradiation intensity: 20 mW/cm$^2$; irradiation time: extended to 2 h at 0.5 h intervals. The absorbance of the MB aqueous solution was measured after centrifugal settlement by V-660 Model (JASCO Corp., Tokyo, Japan).

3. Results and discussions

3.1 Pore properties

Table 1 shows the pore properties of the Pt/TiO$_2$-Bi$_2$O$_3$ samples determined by N$_2$ adsorption-desorption measurement. All the TiO$_2$-Bi$_2$O$_3$ samples showed larger surface areas than that of Bi$_2$O$_3$. The addition of TiO$_2$...
to Bi₂O₃ tended to increase surface areas. Specifically, 0.3Pt/33TiO₂-67Bi₂O₃ and 0.3Pt/36TiO₂-64Bi₂O₃ showed rather large surface areas of 30 and 62 m²/g, respectively. Because 0.3Pt/36TiO₂ is X-ray amorphous, both high surface areas may be related to amorphous phase observed as broad halo patterns around 30° as will be seen in Fig. 1 (a). In the present case, the effect of Pt-loading on pore properties was negligibly small.

### 3.2 Crystallization behavior

Figs. 1 (a) and 1 (b) present the X-ray diffraction patterns of the Pt/TiO₂-Bi₂O₃ and TiO₂-Bi₂O₃ samples, respectively. In the main precipitated phases, the following (i) through (vii) phase changes were observed: (i) α-Bi₂O₃ (JCPDS No. 71-2274) for 0 wt% TiO₂, (ii) α-Bi₂O₃ and Bi₁₂TiO₂₀ (JCPDS No. 34-0097) for 5 wt% TiO₂, (iii) Bi₂₀TiO₃₂ and α-Bi₂O₃ for 9 wt% TiO₂, (iv) Bi₂₀TiO₃₂ (JCPDS: No. 42-0202) and Bi₂TiO₅ (JCPDS: No. 32-0118) for 17 wt% TiO₂, (v) Bi₂₀TiO₃₂ and Bi₂TiO₅ for 23 wt% TiO₂, (vi) Bi₂₀TiO₃₂ and Bi₂Ti₄O₁₁ (JCPDS: No. 15-0325) for 28 wt% TiO₂, (vii) Bi₂₀TiO₃₂ and Bi₂Ti₄O₁₁ (JCPDS: No. 15-0325) for 33 wt% TiO₂ and finally (viii) to the X-ray amorphous phase for 36 wt% TiO₂ with increasing TiO₂ content. The addition of TiO₂ up to and including 28 wt% gave rise to the crystalline phases with relatively higher crystallinity in which however, the 17TiO₂-83Bi₂O₃ and 23TiO₂-77Bi₂O₃ samples alone showed quite lower crystallinity, compared with the Pt-loaded members as shown in Fig. 1 (b) below, whereas the remainder of the samples showed similar diffraction patterns regardless of Pt-loading.

Bi₂TiO₃₂, which is the most familiar bismuth titanate to show high activity for UV irradiation (including both UV and visible irradiation) as well as visible irradiation as well, as this catalytic activity is explained by the following contrasting performance: 0.05Pt/5TiO₂-95Bi₂O₃ and 0.1Pt/9TiO₂-91Bi₂O₃ showing low activity, whereas 0.1Pt/17TiO₂-83Bi₂O₃ and 0.2Pt/23TiO₂-77Bi₂O₃ showing high activity. Moreover, the two diffraction lines observed at around 21 to 23°, which are distinguishable from those of the other crystals, are found small to the same degree, indicating that such a small amount of the Bi₂TiO₃₂ is unlikely to affect photocatalytic activity as seen in Fig. 5 below.

The most interesting result of all obtained is that the Pt-loading 0.1 wt% or higher promotes crystallization of the bismuth titanate such as Bi₂Ti₂O₇ for 17TiO₂-83Bi₂O₃ and 23TiO₂-77Bi₂O₃. Actually, the 23TiO₂-77Bi₂O₃ undergoes the same thermal history as the 0.2Pt/23TiO₂-77Bi₂O₃ has quite lower crystallinity, compared with the Pt-loaded member. This means that crystallization of the 0.2Pt/23TiO₂-77Bi₂O₃ is not just resulting from the heating effect exerted on the Pt-impregnation treatment. As for the 23TiO₂-77Bi₂O₃, the noteworthy effect was observed as seen in Figs. 1 (a) and 1 (b). This is well-grounded, because the 23TiO₂-77Bi₂O₃ (64 mol% TiO₂) is assumed to constitute the intermediate between Bi₂Ti₂O₇ (60 mol% TiO₂) and Bi₂Ti₄O₁₁ (67 mol% TiO₂) which are precipitated by Pt-loading.

| Sample name       | BET          | BJH          |
|-------------------|--------------|--------------|
|                  | SA (m²/g)    | PV (cm³/g)   | PD (nm) |
| Bi₂O₃             | 0.7          | 0.01         | 59      |
| 5Ti-95Bi          | 1.1          | 0.01         | 32      |
| 0.05Pt/5Ti-95Bi   | 1.8          | 0.03         | 76      |
| 9Ti-91Bi          | 2.5          | 0.01         | 26      |
| 0.1Pt/9Ti-91Bi    | 3.0          | 0.02         | 20      |
| 17Ti-83Bi         | 2.7          | 0.03         | 32      |
| 0.1P/17Ti-83Bi    | 2.3          | 0.03         | 49      |
| 23Ti-77Bi         | 7.0          | 0.03         | 16      |
| 0.1Pt/23Ti-77Bi   | 5.1          | 0.02         | 14      |
| 0.2Pt/23Ti-77Bi   | 7.8          | 0.03         | 15      |
| 0.3Pt/23Ti-77Bi   | 6.2          | 0.03         | 19      |
| 28Ti-72Bi         | 13           | 0.02         | 6.5     |
| 0.3Pt/28Ti-72Bi   | 9.3          | 0.02         | 10      |
| 33Ti-67Bi         | 28           | 0.03         | 6.7     |
| 0.3Pt/33Ti-67Bi   | 30           | 0.05         | 7.4     |
| 36Ti-64Bi         | 68           | 0.25         | 15      |
| 0.3Pt/36Ti-64Bi   | 62           | 0.25         | 16      |

*SA: Surface area, PV: Pore volume, PD: Pore diameter
crystalized even if it was not Pt-loaded. Interestingly, on the other hand, effect of Pt-loading on the crystallization for the 36Ti-64Bi (corresponding to 77 mol% TiO₂) was not observed. This means that Pt-loading does not always enhance crystallization. Hence, if the test samples constitute amorphous phase in fraction, and the composition of the sample as in the case of 17TiO₂-83Bi₂O₃ (54 mol% TiO₂) and 23TiO₂-77Bi₂O₃ (64 mol% TiO₂) resembles the corresponding crystals (Bi₂0TiO₃: \(E_g=2.1 \text{ eV} \) 18), Bi₁₂TiO₂₀: \(E_g=2.4 \text{ eV} \) 9), Bi₄Ti₃O₁₂: \(E_g=2.1-2.7 \text{ eV} \) 13), 2.0-2.4 eV 17), 2.1 eV 18) and Bi₂Ti₂O₇: \(E_g=2.6 \text{ eV} \) 15), the foregoing effect of Pt-loading on the promotion of crystallization would be substantiated. Since no remarkable crystallization of bismuth titanate was observed for the 23TiO₂-77Bi₂O₃ which was even heat-treated at 500 °C (Fig. 1 (b)), this will evidently support for promotion effect on crystallization at 300 °C if Pt-loaded. While it is well-known that Pt acts as a nucleating agent in some glasses 24), such Pt role has been for the first time clarified in the present study as far as the for crystallization of bismuth titanate concerned, to the best of our knowledge.

### 3.3 Optical properties

The UV-VIS spectra of the Pt/TiO₂-Bi₂O₃ samples are shown in Fig. 2. The band gap energy was determined from the spectra of these samples obtained. Thus, 5TiO₂-95Bi₂O₃ to 33TiO₂-67Bi₂O₃ showed lower band gap energy levels (2.3-2.4 eV), compared with Bi₂O₃ (2.8 eV). These results are consistent with such reports that the following intermediates (Bi₂0TiO₃: \(E_g=2.1 \text{ eV} \) 18), 2.4 eV 21), Bi₁₂TiO₂₀: \(E_g=2.4 \text{ eV} \) 9), Bi₂0TiO₃: \(E_g=2.6-2.7 \text{ eV} \) 13), \(E_g=2.5-2.7 \text{ eV} \) 18), Bi₂Ti₂O₇: \(E_g=2.1-2.7 \text{ eV} \) 13), 2.0-2.4 eV 17), 2.1 eV 18) and Bi₂Ti₂O₇: \(E_g=2.6 \text{ eV} \) 15)) tend to show narrower band gaps than those of end members of Bi₂O₃: \(E_g=2.8-3.0 \text{ eV} \) 6) and TiO₂: \(E_g=3.0-3.2 \text{ eV} \) 8,13, 16,17,18,20,21). Meanwhile, in the present study, the 0.3Pt/36TiO₂-64Bi₂O₃ sample showed such wider band gap (3.1 eV) as close to those of TiO₂. This may be ascribed to the highest TiO₂ content and the amorphous nature of...
this sample catalyst. The effect of Pt-loading on spectra was negligibly small as seen in 0.1Pt/17TiO2-83Bi2O3, 0.2Pt/23TiO2-77Bi2O3 and 0.3Pt/28TiO2-72Bi2O3. Thus, most of the Pt/TiO2-Bi2O3 samples are considered to be the visible light-driven photocatalyst candidates.

Fig. 3 shows the PL spectra of the Pt/TiO2-Bi2O3 samples (Ex=310 nm). The peaks observed at around 420 nm for the Pt/TiO2-Bi2O3 samples tended to decrease with TiO2 content increasing up to and including 23 wt%, whereas further addition of TiO2 tended instead to increase the PL intensity. In common with all the TiO2-Bi2O3 samples, Pt-loading tended to decrease the PL intensity, which means that the recombination sites between electrons and holes are restricted. This is one of key factors to enhance the photocatalytic activity.

3.4 Photocatalytic activity

Fig. 4 shows the typical change in absorption spectra of the MB aqueous solution for 0.2Pt/23TiO2-77Bi2O3 observed before (-30 to 0 min in the darkness) and after 30 to 120 min under visible light irradiation. The appreciable decrease in absorbance of the MB aqueous solution occurred after 30 min irradiation.

The effect of Pt and TiO2 contents on MB degradation (after 2 h visible light irradiation) of the Pt/TiO2-Bi2O3 samples is given in Fig. 5 in which at first, the TiO2-Bi2O3 samples (0Pt in Fig. 5) hardly showed any photocatalytic activity for the MB degradation. As the Pt-loading is known to often enhance photocatalytic activity for the MB degradation, as expected from the relevant PL spectra obtained in the present study, the Pt-loading actually played a key role in the enhancement of photocatalytic activity by the restricting the recombination of the photo-induced electron and hole pairs, and the optimum Pt content (0.05-0.3 wt%) and TiO2 content (17-28 wt%) were observed, respectively in the photocatalytic activity for the MB degradation on Pt/TiO2-Bi2O3. The amount of optimum Pt-loading increased from 0.05 wt% to 0.3 wt% with increasing TiO2 content. This may be related to such findings in the present study that the TiO2-Bi2O3 samples with higher TiO2
content tend to show larger surface areas. In other words, larger amount of Pt-loading onto the TiO$_2$-Bi$_2$O$_3$ samples having smaller surface areas gives rise to the aggregation of loaded Pt, eventually inhibiting the enhancement of the separation of the photogenerated electrons-holes pairs.

Specifically, the 0.1Pt/17TiO$_2$-83Bi$_2$O$_3$, 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ and 0.3Pt/28TiO$_2$-72Bi$_2$O$_3$ samples showed the highest photocatalytic activity under each Pt content controlled when TiO$_2$ content was controlled and changed under the same Pt content as shown in Fig. 5, while only the Bi$_2$Ti$_2$O$_7$ was retained as a common phase in these samples. As the Bi$_2$Ti$_2$O$_7$ is the familiar photocatalyst with higher activity under UV irradiation and visible irradiation as well. It is reported that the bond angle of Ti-O-Ti in the Bi$_2$Ti$_2$O$_7$ is close to ideal 180°, so it might facilitate the movement of photogenerated electron-hole pairs and eliminate the recombination of electron-hole pairs to eventually increase the catalytic activity. In the present study, the Bi$_2$Ti$_2$O$_7$ is considered a key crystalline phase for the photocatalytic activity.

Thus, the highest photocatalytic activity of the 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ obtained may be ascribed to the largest amount of Bi$_2$Ti$_2$O$_7$ component. Interestingly, the 17TiO$_2$-83Bi$_2$O$_3$ and 23TiO$_2$-77Bi$_2$O$_3$ samples are found to have quite lower crystallinity, compared with the Pt-loaded members, and at the same time, these samples showed lower PL intensity to the same degree regardless of Pt-loading. Hence, the Pt-loading is verified to play a key role in the enhancement of photocatalytic activity as a nucleating agent of bismuth titanate, whereas the 28TiO$_2$-72Bi$_2$O$_3$ before and after Pt-loading showed similar XRD patterns and PL intensity that may have largely been decreased by Pt-loading.

The effect of UV cut filter on photocatalytic activity of the 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ was investigated using sharp cut filter (L42) to clarify the visible light response. The MB degradation of TiO$_2$ (P25) was rated 98% and 62% for the test without and with the filter L42, respectively, whereas the MB degradation of 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ was rated 92% irrespective using the cut filter. This means that the 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ can utilize the light having the wavelength longer than that of TiO$_2$ (P25).

Consequently, the effect of Pt-loading on the photocatalytic activity can be attributed to the following two factors (1) the restriction of recombination of the photo-induced electron and hole pairs by Pt, and (2) the promotion of crystallization of bismuth titanate such as Bi$_2$Ti$_2$O$_7$ under the high photocatalytic activity provided by the amorphous TiO$_2$-Bi$_2$O$_3$.

Finally, it should be noted that the 33TiO$_2$-67Bi$_2$O$_3$ and 36TiO$_2$-64Bi$_2$O$_3$ samples with quite larger surface areas showed the lower photocatalytic activity for the MB degradation. The lower crystallinity or amorphous nature characteristic of these samples were considered to counteract the enhancement of the photocatalytic activity with their large surface areas.

4. Conclusions

In this reported study, the Pt/TiO$_2$-Bi$_2$O$_3$ test catalysts were prepared by impregnating Pt on the sol-gel derived TiO$_2$-Bi$_2$O$_3$ to give these testpieces high photocatalytic activity under visible light irradiation. In particular, the effects of the adding TiO$_2$ to Bi$_2$O$_3$ and loading Pt on TiO$_2$-Bi$_2$O$_3$ have been investigated in respect of the photocatalytic MB degradation under visible light irradiation. The following results were obtained:

(1) The optimum Pt support content (0.05-0.3 wt%) and TiO$_2$ content (17-28 wt%) were observed in the photocatalytic activity for the MB degradation on Pt/TiO$_2$-Bi$_2$O$_3$. Specifically, the 0.1Pt/17TiO$_2$-83Bi$_2$O$_3$, 0.2Pt/23TiO$_2$-77Bi$_2$O$_3$ and 0.3Pt/28TiO$_2$-72Bi$_2$O$_3$ samples showed relatively higher photocatalytic activity for the MB degradation.

(2) The amount of optimum Pt-loading increased from 0.05 wt% to 0.3 wt% with increasing TiO$_2$ content. This may be related to the surface areas characteristic of the TiO$_2$-Bi$_2$O$_3$ samples.

(3) The effects of Pt-loading on the photocatalytic activity can be attributed to the following two factors (1) the restriction of recombination of the photo-induced electron and hole pairs by Pt, and (2) the promotion of crystallization of bismuth titanate such as Bi$_2$Ti$_2$O$_7$ under the high photocatalytic activity provided by the amorphous TiO$_2$-Bi$_2$O$_3$.

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