Scientific
Research

Crystal Growth of ZnO Microneedles in Water Containing Microbubbles

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Abstract

Microbubble technology is now available in a wide range of industrial fields. The liquid containing microbubbles possesses a large number of air-liquid interfaces, and also generates radicals during bubble collapse. Here, we synthesized ZnO powder to explore the potential of microbubbles as starting materials for the formation of crystalline micro- or nanoparticles. The bubbles facilitated the growth of ZnO microneedles in high yields, and enhanced the reaction by radicals generated on bubble collapsing.

Keywords

Microbubble, Microcrystal, ZnO

1. Introduction

Microbubbles are defined as having diameters less than 50 μm, and have important technical applications in industrial fields [1]-[3]. Although the characteristics of water that contains microbubbles are not completely understood [3]-[5], such water is currently used in semiconductor plants to remove oil [6] and on Japanese highways to remove de-icing salts [7].

Microbubbles can be generated in water by various methods. One of the most efficient methods for producing fine bubbles, such as nano- or microbubbles, involves centrifugal gas-liquid separation [8], in which a mixture of gas and liquid is rotated at a high rotational velocity. The gas bubbles in the liquid are fractured because of the centrifugal shearing force during rotation. Advantages of this method include the generation of bubbles of ~100 nm in diameters and the long-term stability [9]. Additionally, the gas-liquid shearing method is versatile because any gas and liquid can be used as starting materials.

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Microbubbles tend to decrease in size due to the dissolution of their interior gas into the surrounding water, and to collapse due to the high interior gas pressure on collapsing. Free radicals are generated from the bubbles even in the absence of ultrasound waves. These free radicals are known to accelerate chemical reactions. Indeed, the radicals generated by cavitation are used in sonochemistry [10]. Moreover, such radicals have affected the crystal growth of ZnO [11], in which ZnO nanorods were aligned on a substrate. On the other hand, it was expected that microbubbles could act as crystal nuclei for the heterogeneous nucleation because of the high interfacial surface area between the bubbles and the liquid. From the view point of crystal growth, the advantage of using microbubble nucleation would be the absence of residue in the final product.

A preparative approach employing microbubbles would constitute a novel preparation method for nanomaterials. However, no reports are presently available. Here, we synthesize ZnO microcrystals using water containing microbubbles (MB water), in order to demonstrate its potential in the field of nanomaterials.

2. Experimental Section

MB water was prepared by the centrifugal gas-liquid separation method (BUVITAS HYK-32-D, Ligaric, Japan [7]. Distilled water (11 L) at a flow rate of 45 L/min and gas at a rate of 0.7 L/min were subjected to centrifugal rotation for 90 min to afford MB water. The gases used in this study were N_2 and O_3; the latter was generated by UV irradiation of oxygen gas (EO-OG-R4, Ecodesign-labo, Japan). It should be noted that O_3 MB water contains both O_2 and O_3 gases.

The concentration of ozone in O_3 MB water was determined by the difference in the UV absorption between the purified and ozonated water (ozone densitometer OZM 5000G, Okitrotec Co. Ltd., Japan).

The size distributions of the gas bubbles in the purified and MB waters were characterized using a laser-illuminated optical microscopic technique based on particle-tracking analysis (NanoSight LM10, NanoSight, Ltd.) [12]. The detection limit ranged from 50 to 1000 nm, depending on the particles and solvent.

All chemical reagents were used without further purification. Solutions of $Zn(NO_3)_2$ (25 mM) and of hexamethylenetetramine (HMT, 25 mM) were prepared using different water medium (purified water without bubbles for comparison, N_2 MB water, or O_3 MB water), $Zn(NO_3)_2$ (Wako Pure Chemicals Industries, Ltd., Japan), and HMT (Wako Pure Chemicals Industries, Ltd., Japan). A mixture of $Zn(NO_3)_2$ solution (50 mL) and HMT solution (50 mL) was stirred for 90 min at 90°C to produce a precipitate. Microparticles were collected on a Si substrate by dipcoating.

Scanning electron microscopy (SEM) images were obtained for the microparticles using a field-emission scanning electron microscope (JSM6500F, JEOL, Japan). X-ray diffraction (XRD) patterns were also obtained for the precipitate (RINT-2000, Rigaku, Japan).

3. Results and Discussion

Figure 1 and **Figure 2** show the time dependence of the mode values of the diameter and the bubble concentration (10^8 particles/mL) at the mode value of the diameter, respectively. The error bars indicate the standard dev-
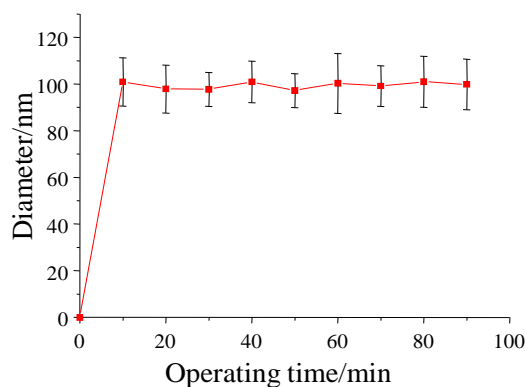

Figure 1. Mode value of the N_2 bubble diameter versus centrifugal gas-liquid separation time. The error bars indicate the standard deviation over seven experiments.
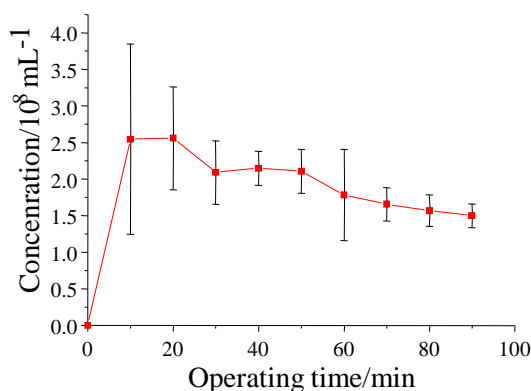
Figure 2. Bubble concentration (10^8 particles/mL) at the mode values of the diameter for N_2 MB water versus centrifugal gas-liquid separation time. The error bars indicate the standard deviation for over seven experiments.

iation over seven repetitions. The bubbles in the water were determined to be microbubbles of ~100 nm in diameter after 10 min operation. The standard deviation of the concentration before 30 min was rather large, but became small after 30 min. Moreover, over 50 min, the concentration decreased due to the heat generated by the centrifugal apparatus. Therefore, because of the stability of both the diameter and concentration, N_2 microbubble (MB) water centrifugally rotated for 50 min was used for the preparation of ZnO.

In the case of O_3 MB water, the bubble diameters showed similar behavior to the N_2 MB water. However, the ozone concentration reached a maximum and then decreased after ~30 min (**Figure 3**). This was also due to the heat generated by the centrifugal apparatus, because the ozone spontaneously decomposed above room temperature. Therefore, because of the stability of the concentration, O_3 MB water operated for 50 min was used for the preparation of ZnO.

Table 1 shows the reaction yields of ZnO together with the bubble concentrations, the maximum bubble diameter values, and the ozone concentration. The ZnO yields obtained from purified water, N_2 MB water, and O_3 MB water were 0.11, 0.35, and 0.60, respectively. Thus, the yield was increased by using the MB waters instead of pure water, and the O_3 MB water produced a much higher yield than the N_2 MB water.

The increase in the yield through the use of MB water can be interpreted based on the growth mechanism of ZnO nanorods as follows [13]-[15],

$$\left(CH_2\right)_6 N_4 + 6H_2O \rightarrow 4NH_3 + 6HCHO \tag{1}$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \tag{2}$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \tag{3}$$

In the case of MB water, Reaction (3) was expected to be enhanced due to the increased interfacial surface area between the bubbles and water.

In the case of O_3 MB water, the increment can be also interpreted based on the generation of radicals on O_3 decomposition. That is, ozone decomposes to generate free radicals as follows [16],

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{4}$$

$$O_3 + HO_2^- \rightarrow HO\bullet + \bullet O_2^- + O_2 \tag{5}$$

where the symbol "•" indicates the radical. The generated radical reacts with Zn^{2+} to produce ZnO as follows [11],

$$Zn^{2+} + 2\bullet O_2^- \rightarrow ZnO + 3/2 O_2 \tag{6}$$
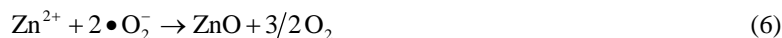
XRD measurements were carried out to examine whether the microbubbles affected the ZnO crystal structure or not. **Figure 4** shows XRD patterns of ZnO prepared using purified water, N_2 MB water, and O_3 MB water,
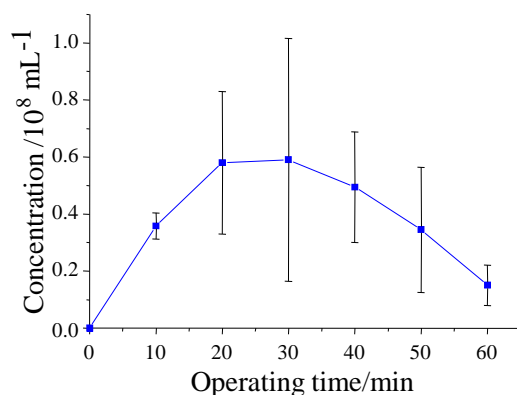
Figure 3. Aqueous ozone concentration in water plotted against the operation time. The error bars indicate the standard deviation for over seven experiments.
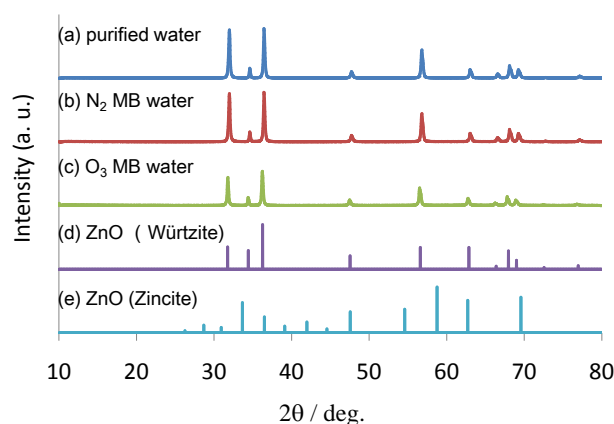

Figure 4. XRD patterns of ZnO prepared with (a) purified water, (b) N_2 MB water, or (c) O_3 MB water, together with XRD patterns derived from the JCPDS database.

Table 1. Bubble concentration, mode value of the diameter, ozone concentration, and reaction yields.

	Purified water	MB water	
		N_2	O_3
Bubble concentration/10^8 mL^{-1}	0	1.64	0.88
Bubble diameter/nm	-	103	135
Aqueous ozone concentration/mgL^{-1}	-	-	3.19
yield ([ZnO]/[Zn(NO$_3$)$_2$])	0.11	0.35	0.6

together with the powder diffraction patterns of wurtzite and zincite from the JCPDS database. The results clearly showed that there were no differences among the samples. Hence, neither the interfacial surfaces nor the radicals had distinct effect on the crystal structure of ZnO.

Finally, SEM observations were carried out to determine the effects of the microbubbles on the sizes or shapes of ZnO crystals (**Figure 5**). From purified water, the island-shaped ZnO crystals were grown, while in the cases of water with microbubbles, the ZnO crystals in needle-like structures of ~1 μm in length were grown. Note that purified water has no interfacial surfaces in the reaction system. As a result, the mechanism of crystal growth is mainly due to homogeneous nucleation. The number of initial crystallites is small, which results in large crystals and a low reaction yield. On the other hand, in the MB water, a lot of interfacial surfaces are present in the reac-
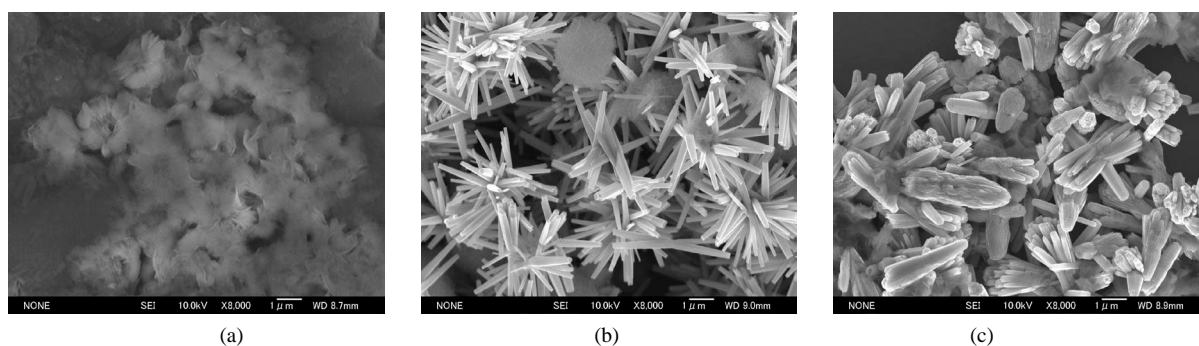
(a)   (b)   (c)

Figure 5. SEM images of ZnO prepared with (a) purified water, (b) N_2 MB water, and (c) O_3 MB water.

tion system, which acts as nuclei for heterogeneous nucleation. The number of ZnO crystallites is expected to be large. Accordingly, the concentration of Zn^{2+} decreased rapidly, resulting in small crystals and high yields. In addition, from O_3 MB water, ZnO crystals with low aspect ratio were grown, while in the case of N_2 MB water, that with high aspect ratio. We believe that this result is due to the enhancement of the oxidation reaction by O_3.

4. Conclusions

ZnO crystals were grown from purified water, N_2 MB water, and O_3 MB water mediums. On the basis of the yield, crystal structure, and crystal shape, we reviewed whether the presence of the bubbles and radicals affected crystal growth. The yields in the experiments that used MB water were larger than in those that used purified water. We believe that this increment by means of MB water was due to the presence of interfacial surfaces between the bubbles and water, which acted as nuclei for heterogeneous nucleation. O_3 MB water provided a higher yield than N_2 MB water. This increment was likely due to the radicals generated by O_3. The use of MB water resulted in the formation of ZnO with needle-like structures of ~1 μm in length, whereas that of purified water produced island-shaped ZnO. This result was also interpreted as being due to heterogeneous nucleation: the concentration of Zn^{2+} decreased rapidly, resulting in small crystals. On the other hand, the crystal structures were identical and independent of the presence of MB in the initial water. Thus, MB water is a potential and novel starting material for the facile preparation of microcrystals.

We have presented a simple and facile method for producing ZnO microneedles using water containing microbubbles. In the reaction system, the interfaces between the bubbles and water are expected to promote heterogeneous nucleation. In addition, the radicals generated on the collapse of O_3 bubbles can be used as oxidizing agents. We expect that the present process can also be applied to the synthesis of other types of oxide nano- or microparticles because we can select any gas as inert, oxidative or reductive gas for preparing bubbles.

Acknowledgements

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