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Synthesis of Submicrometer Zinc Oxide Particles and Zinc Oxide Nanowires Using Microwave Irradiation

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The synthesis of submicrometer zinc oxide (ZnO) particles by a microwave-assisted sol–gel reaction in a non-alcoholic solvent was investigated. ZnO particles were rapidly prepared by the microwave-assisted sol–gel reaction of zinc acetate dihydrate, which is an inorganic monomer, with distilled water in N,N-dimethylacetamide as a solvent. ZnO particles that were prepared from zinc acetate dihydrate by the sol–gel reaction were changed into ZnO nanowires after microwave irradiation.

Keywords: Sol–gel | Zinc oxide | Microwave irradiation

Zinc oxide (ZnO) is a semiconductor with a large band gap of $E_g = 3.37$ eV, exhibiting near UV emission, transparent conductivity, and piezoelectricity. Furthermore, ZnO is bio-safe and non-toxic. Therefore, ZnO is a technologically important material. For example, ZnO is used as a varistor and contains several other elements in small amounts.\(^1\) ZnO particles offer considerable potential as starting materials. In addition, ZnO particles have various applications such as transparent UV-protection films and chemical sensors. In recent years, doped ZnO has been researched as a conductive filler\(^2\) and ITO-alternative material.\(^3-5\) Therefore, ZnO has attracted attention as a novel and interesting material. Various methods have been developed for the synthesis of ZnO with various morphologies and size, such as the sol–gel reaction,\(^6\) chemical vapor deposition,\(^7-9\) chemical vapor deposition\(^10,11\) and polymer stabilization.\(^12\) The sol–gel reaction, which is an excellent method for the synthesis of ZnO, is of considerable interest as a synthetically flexible, low-temperature approach for the fabrication of metal and semi-metal oxide glasses and ceramics. The sol–gel reaction can generally lead to the formation of fine powders in solvent. We have been investigating the sol–gel reaction utilizing microwave irradiation. For example, monodispersed submicrometer silica silicon spheres were rapidly prepared by a microwave-assisted sol–gel reaction using tetramethoxysilane as a tetrafunctional alkoxysilane. In the case of the microwave-assisted sol–gel reaction of methyltrimethoxysilane as a trifunctional alkoxysilane, cubic octamethylcyclotetrasiloxane can be obtained in a good yield when the microwave-assisted sol–gel reaction is used.\(^13\) Thus, the microwave-assisted sol–gel reaction is able to dramatically reduce the reaction time from hours to minutes, and can increase product yield and enhance product purity. Because of increasing environmental concerns, green chemistry has been receiving progressively more attention after the 1990s.\(^15-17\) Therefore, there is a great need to advance novel methodologies for chemical reactions using environmentally eco-friendly methods. From the viewpoint of green chemistry, microwave-assisted synthesis may be meaningful to reduce energy use. Herein, we wish to describe the result of the synthesis of submicrometer ZnO particles by the microwave-assisted sol–gel reaction (Scheme 1). We also describe the result of the synthesis of ZnO nanowires that were prepared from submicrometer ZnO particles after microwave irradiation.

Microwave irradiation experiments were performed using a microwave oven (SANYO EMO-FZ40). The reaction was carried out in a 100 mL PTFE beaker placed at the center of the microwave oven. Into the beaker, 60 mL of N,N-dimethylacetamide (DMAc) was poured and 0.50 g of zinc acetate dihydrate (Zn(OAc)$_2$·2H$_2$O) was added. To dissolve Zn(OAc)$_2$·2H$_2$O, the mixture was stirred at 60°C for 15 min. Then, the solution was cooled rapidly to 15°C. Subsequently, 1 mL of distilled water was poured into the solution. The beaker was placed at the center of the microwave oven where the solution was irradiated by 100 W. To evaluate the effect of microwave irradiation time, the experiments were carried out at different periods of exposure to irradiation (Table 1).

Only 1.5–4.0 min of microwave irradiation resulted in a white suspension (Table 1, Runs 2–7). The temperature of the reaction mixture was 64–118°C after 1.5–4.0 min of microwave irradiation. A conventionally heated suspension was also prepared for comparison with microwave treatment (Table 1, runs 1).

### Table 1. Synthesis of ZnO particles using microwave irradiation

<table>
<thead>
<tr>
<th>Run</th>
<th>Time (min)</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
<th>PS (%nm$^a$)</th>
<th>PS (%nm$^b$)</th>
<th>FWHM (%$^{f,b}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>53</td>
<td>0</td>
<td>ND$^c$</td>
<td>ND$^c$</td>
<td>ND$^c$</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>64</td>
<td>31</td>
<td>312 ± 60</td>
<td>275 ± 21</td>
<td>0.741</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>75</td>
<td>65</td>
<td>404 ± 58</td>
<td>284 ± 15</td>
<td>0.718</td>
</tr>
<tr>
<td>4</td>
<td>2.5</td>
<td>86</td>
<td>73</td>
<td>437 ± 63</td>
<td>320 ± 15</td>
<td>0.694</td>
</tr>
<tr>
<td>5</td>
<td>3.0</td>
<td>98</td>
<td>78</td>
<td>485 ± 63</td>
<td>328 ± 17</td>
<td>0.624</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>108</td>
<td>48</td>
<td>509 ± 66</td>
<td>352 ± 60</td>
<td>0.471</td>
</tr>
<tr>
<td>7</td>
<td>4.0</td>
<td>118</td>
<td>19</td>
<td>ND$^c$</td>
<td>ND$^c$</td>
<td>0.400</td>
</tr>
<tr>
<td>8</td>
<td>20.0$^e$</td>
<td>98</td>
<td>78$^b$</td>
<td>445 ± 106$^b$</td>
<td>489 ± 72$^b$</td>
<td>0.729$^b$/0.706$^b$</td>
</tr>
</tbody>
</table>

$^a$Conditions: Zn(OAc)$_2$·2H$_2$O 0.50 g, catalyst (H$_2$O) 1.0 mL, DMAc 60 mL. $^b$Particle size by SEM images. $^c$Particle size by DSL analysis. $^d$The full width at half-maximum of (102) (2θ = 47.5°). $^e$Not determined. $^f$Oil bath heating. $^g$The yield (78%) is total yield of the ZnO particles obtained from the filtrate (38%) and the solid ZnO which remained on the filter paper (40%). $^h$The ZnO particles were obtained from the filtrate. $^i$The solid ZnO remained on the filter paper.

\[ \text{Zn(OAc)$_2$·2H$_2$O} \xrightarrow{\text{MW (100 W)}} \text{ZnO particles} \]
Run 8). After microwave irradiation, the reaction mixture was poured into diethyl ether. The white solid was separated by centrifuging at 3000 rpm for 10 min. For all samples, the obtained solids were washed with hot ethanol and centrifuged at 3000 rpm for 10 min. The obtained precipitate was suspended in ethanol. The resulting suspension was filtrated by a filter paper (1.0 µm). The filtrate was separated by centrifugation at 3000 rpm for 10 min. The obtained precipitate was dried under reduced pressure, and then subjected to scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses.

Figure 1 shows SEM images of the obtained white solids. In the case of 1.5–3.5 min of microwave heating (Figures 1a–1e), the observed particles were nearly spherical, with particle sizes in the range of 300–510 nm in diameter. As the microwave irradiation time increased, the particle size and yield increased. In the case of more than 4.0 min irradiation, spherical particles were hardly found in the SEM image (Figure 1f). In the case of conventional heating, nearly spherical particles were observed (Figure 1g). However, the yield of the particles obtained from the filtrate was not so high. Therefore, the white solid that remained on the filter paper was observed by SEM. As a result, it was found that appeared to be aggregate particles (Figure 1h).

The yield of particles obtained from the filtrate might be decreased, because aggregate particles could not be filtered. Compared with the microwave irradiation method, the particle size distribution of the samples that were prepared by oil bath heating was broad (Table 1, Run 8). Therefore, it was clear that the use of microwave irradiation was effective to obtain particles with a narrow particle size distribution. Table 1 shows the results of the average diameters of the obtained particles. From SEM images, the particle sizes were found to be 312–509 nm. The average diameters of the samples prepared by 1.5–3.5 min microwave irradiation were 275–352 nm from DLS analyses. In all cases, the results may be due to differences in refractive index depending on the solute such as partially hydrolyzed Zn(OAc)$_2$·2H$_2$O, DMAC, or H$_2$O. From these results, particle sizes increased as the microwave irradiation time increased, i.e., the particles grew after microwave irradiation. The obtained particles were examined by XRD analysis. The XRD patterns of the obtained particles were in agreement with the patterns of the authentic ZnO sample.

In Table 1, the full width at half-maximum (FWHM) of the (102) reflection of the obtained ZnO particles became narrower as the microwave irradiation time increased. Consequently, ZnO particles with a high FWHM indicate that microwave irradiation can be used to change ZnO into more highly crystalline particles. For comparison, the change in the crystallinity of the ZnO particles prepared by conventional oil bath heating was investigated after microwave irradiation.

ZnO particles (0.10 g) were placed in DMAC (30 mL) at the center of a microwave oven. The irradiated ZnO particles were examined by XRD analysis (Figure 2). The FWHM of the (102) reflection of the irradiated ZnO particles became narrower as the microwave irradiation time increased. In particular, in the case of 6.0 min irradiation, the FWHM was considerably narrower (Figure 2d). This result suggests that the ZnO particles were able to change into a more highly crystalline structure under microwave irradiation. In the case of 6.0 min irradiation without a solvent, the FWHM of (102) changed considerably (Figure 2e and Table 2).

Figure 3 shows the SEM images of the irradiated ZnO particles. In the case of 2.0 and 4.0 min of microwave irradiation (Figures 3b and 3c), the observed particles were nearly spherical, with particle sizes in the range of 190–210 nm in diameter. When the ZnO particles were irradiated in DMAC for

<table>
<thead>
<tr>
<th>Run</th>
<th>Time /min</th>
<th>Solvent</th>
<th>Temp /°C</th>
<th>PS /nm$^2$</th>
<th>FWHM /°a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>—</td>
<td>—</td>
<td>210 ± 35</td>
<td>0.882</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>DMAc</td>
<td>109</td>
<td>204 ± 29</td>
<td>0.871</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>DMAc</td>
<td>138</td>
<td>190 ± 27</td>
<td>0.741</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>DMAc</td>
<td>137</td>
<td>127 ± 25$^2$/1334 ± 406$^2$</td>
<td>0.329</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>None</td>
<td>ND$^4$</td>
<td>185 ± 34</td>
<td>0.765</td>
</tr>
</tbody>
</table>

$^a$Conditions: ZnO particles were prepared by the sol-gel reaction of Zn(OAc)$_2$·2H$_2$O (2.50 g) in DMAc (300 mL) and distilled water (5.0 mL) with oil bath heating (20 min). $^b$Particle size by SEM images. $^c$The full width at half-maximum of (102) (29 = 47.5°). $^d$The diameter of the obtained ZnO nanowires. $^e$The length of the obtained ZnO nanowires. $^f$Not determined.
6.0 m, ZnO nanowires were obtained. The average length and diameter of the obtained ZnO nanowires were about 1334 and 127 nm, respectively (Figure 3d). On the other hand, when the ZnO particles were irradiated without DMAC for 6.0 min, ZnO nanowires were not obtained (Figure 3e).

Chin et al. have reported the synthesis of ZnO nanowires using a sol–gel reaction of Zn(OAc)$_2$ in the aliphatic amine. In contrast, in our study, it is very characteristic that ZnO particles were rapidly changed into ZnO nanowires after microwave irradiation.

In summary, submicrometer ZnO particles were rapidly prepared after microwave irradiation by the sol–gel reaction of zinc acetate dihydrate with an aqueous solution, in diglyme as a solvent. Moreover, the obtained ZnO particles were changed into ZnO nanowires after microwave irradiation. ZnO nanoparticles and ZnO nanowires have a wide range of potential applications, for example, in solar cells, light-emitting diodes, field-effect transistors, field-emission displays, and biosensors. Since it is expected that ZnO particles and ZnO nanowires can be used in various fields, our eco-friendly method should make it simpler to synthesize them.

Supporting Information is available on http://dx.doi.org/10.1246/cl.160081.

References and Notes
18 Such ZnO nanowires were also prepared from zinc acetate in oleylamine under microwave irradiation. The Supporting Information provides information about the synthetic procedure and spectroscopic data for the obtained ZnO nanowires.