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Solution plasma synthesis of ZnO flowers and their photoluminescence properties

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ABSTRACT

ZnO nanoflowers, amorphous ZnO nanospheres and metallic Zn particles have been controllably synthesized using solution plasma technique at different reaction temperatures and agitation. X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that ZnO nanoflowers were synthesized at a high electrolyte temperature in a static system (no agitation). On the other hand, the use of agitation led to both amorphous ZnO nanospheres and spherical metallic zinc particles. The excitation temperature of plasma was 4000 K from the light emission using spectrometer. From these result, melting and vaporization of the Zn electrode produced particles. ZnO nanoflowers grew on the surface of spherical particles by precipitation from $Zn(OH)_4^{2-}$ ions. Photoluminescence (PL) measurement indicated that as-synthesized ZnO flowers and amorphous ZnO nanospheres showed strong green emissions, which was attributable to their surface defect structure. Furthermore, the annealing at 700 °C led to a reduction in green emissions, attributable to a decrease in the number of surface defects. Photocatalytic activity of ZnO nanoflowers was increased by the annealing.

1. Introduction

Zinc oxide (ZnO) has a wide direct band gap and a large exciton binding energy (3.37 eV and 60 eV, respectively, at room temperature), which make it an important electronic and photonic semiconductor. It has been demonstrated that ZnO is useful in a wide range of applications, including solar cells, ultraviolet lasers, light-emitting diodes, transparent conductors, photocatalytic materials, gas sensors, and luminescence materials. Various ZnO nanostructures, such as nanorods, nanowires, nanospheres, nanodisks, and nanoflowers, have been fabricated by thermal evaporation [1,2], hydrothermal synthesis [3–5], solution routes [6,7], microwave irradiation [8,9], vapor–liquid–solid growth [10], pulsed laser ablation [11,12], plasma [13,14], and electric discharge [15–17].

While there are several ZnO nanostructures, the flower-like morphology, as a special three-dimensional structure, has received the most attention in recent years because of its unique photoluminescence (PL) and photocatalytic properties [5,18,19]. The optical and electrical properties of ZnO are related to its structural defects. It has been reported that the visible emission of ZnO is mainly related to intrinsic defects such as oxygen vacancies (V_o), interstitial oxygen (O_i), zinc vacancies (V_{Zn}) and interstitial zinc (Zn_i) [20]. These defects can affect photocatalytic performance; that is, acting as active centers, they can capture photo-induced electrons, thereby inhibiting the recombination of photo-induced electrons and holes [5].

Recently, the synthesis of ZnO, CuO and SnO nanocrystals using a solution plasma technique was reported [21–23]. In our previous study, ZnO nanoflowers precipitated from $Zn(OH)_4^{2-}$ ions [21]. However, the mechanism of oxide nanoflower formation via solution plasma has not been investigated thoroughly. In addition, the photoluminescence and photocatalytic properties of ZnO nanoflowers are not yet fully understood, in spite of their importance. To investigate this further, in the present study, the effects of electrolyte temperature and agitation, which we expected to affect the stability of $Zn(OH)_4^{2-}$ ions, were examined. In addition, the photoluminescence and photocatalytic properties of the products and the effect annealing were studied, in an effort to determine the types of defects present.

2. Materials and methods

As reported previously [21], the experimental setup consisted of two electrodes in a glass cell. The cathode comprised a Zn wire (diameter: 1.0 mm; purity: 99.99%) placed at the center of the cell. Voltage was applied using a direct current power supply (ZX800H, Takasago). The electrolyte was a 0.5 M K_2CO_3 solution,

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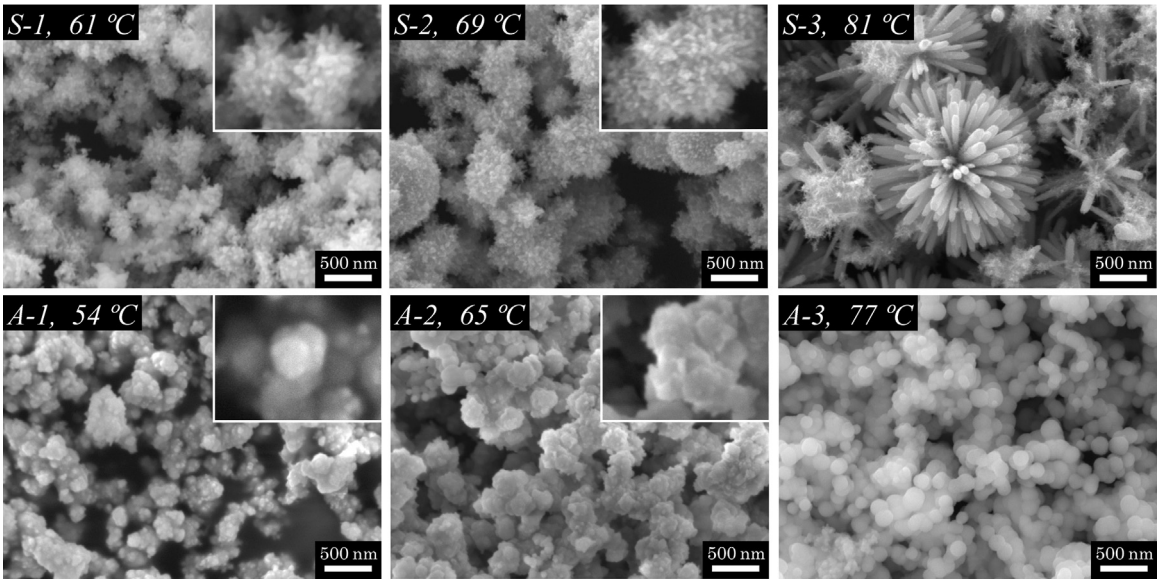

Fig. 1. SEM images of the products made with and without agitation at different electrolyte temperatures. The labels show the average solution temperatures during electrolysis.

Table 1
Experimental conditions.

Sample name	Agitation	Temperature control
S-1	No	Cooling using 25 °C water
S-2		Cooling using 25 °C water
S-3		Cooling in air
A-1	1500 rpm	Cooling using 25 °C water
A-2		Cooling in air
A-3		Heating using a hotplate

with a purity of 99.5%. The electrolyte temperature was measured at a depth of 10 mm using a polymer-coated thermistor (Ondotori TR-71Ui, T&D). The current and voltage were measured using the DC power supply. The light emission from plasma was measured using a visible light spectrophotometer (USB 2000+, Ocean Optics). Experimental conditions for studying the effects of agitation and electrolyte temperature on nanoparticle formation are shown in Table 1. The "S" in the sample name means static conditions (i.e., without agitation), and "A" signifies that agitation was employed. Agitation, applied using a magnetic stirrer, was set at 1500 rpm.

The solution plasma method employed was as follow. After heating the solution to 60 °C, the applied voltage was increased from 0 to 80 V at a rate of 0.5 V s^{-1}, then maintained at 80 V for one hour. During electrolysis, the reaction temperature was fixed by controlling the electrolyte temperature as shown in the Table 1. The temperature was changed stepwise in three steps using water at 25 °C and a hotplate. Afterward the products were collected by centrifugation, then washed with deionized water. Subsequently, the products were characterized using a JSM-7001FA (JEOL) scanning electron microscope (SEM), a Miniflex II (Rigaku) X-ray diffractometer (XRD), and a JEM-2010F (JEOL) transmission electron microscope (TEM). Photoluminescence (PL) measurements were performed at room temperature using a Xe lamp line (FP-6400, JASCO) at a wavelength of 325 nm. The photocatalytic activities of the products were determined by measuring the rate of degradation of methylene blue under UV light, at an applied power of 30 W. In a typical photocatalytic experiment, 40 mg of dried product was added to 200 ml of a solution of 5.0×10^{-4} mg L^{-1} methylene blue in water. The mixture was first sonicated for 12 h in the dark to reach the adsorption equilibrium, then irradiated with UV light at room temperature. Before and after UV irradiation, the concentration of methylene blue was measured using a visible light spectrophotometer (USB 2000+ USB-ISS-VIS, Ocean Optics).

3. Result and discussion

3.1. Effects of temperature and agitation

Experimental results are shown in Table 2. The current was increased at high temperatures. As we observed in previous work, at high temperature a gas layer completely covered the electrode, preventing current flow [24]. High current flow led to production of a large amount of particles.

SEM images and XRD patterns of the products are shown in Figs. 1 and 2, respectively. From the XRD results, the ratio of ZnO to Zn increased with increasing temperature under static conditions. Sample S-3 contained primarily ZnO nanoflowers, with only a small number of Zn particles, while S-1 consisted solely of Zn particles. Sample S-2 contained many horn-shaped structures on the particle surfaces, which grew into the rod-shaped structures seen in S-3. According to the TEM observation, rod-like crystals grew in the [0 0 0 1] direction on the surface of the spherical particles (see supporting information). The peaks acquired became sharper with increase in the temperature of the solution from which the samples were prepared, indicating that samples with a greater degree of crystallinity were obtained at higher temperatures. The crystallite

Table 2
Summary of the experimental results. The temperature and power are the average values. The amount of nanoparticles produced (Production) was calculated from the difference in the weight of the electrode before and after the experiment.

Sample	Temperature (°C)	Power (W)	Current (A)	Production (mg)
S-1	61	92	1.15	35.3
S-2	69	86	1.08	22.0
S-3	81	52	0.65	24.3
A-1	54	97	1.21	20.1
A-2	65	74	0.93	20.0
A-3	77	51	0.64	13.5