doi:10.1246/cl.2010.783
Published on the web June 19, 2010

Preparation of Zinc Oxide Nanoparticles by Using Microwave-induced Plasma in Liquid

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As a rapid and easy liquid process for preparation of ZnO nanoparticles, we propose here a microwave-induced plasma in water. Generation of plasma in liquid has been achieved at atmospheric pressure without external gas bubbling. After only several minutes of microwave irradiation, about 0.3 g of ZnO nanoparticles was obtained from an aqueous solution of zinc(II) acetate under alkaline conditions.

Inorganic nano- and fine-particles show a wide variety of unique spectroscopic, electronic, chemical, and physical properties.[1,2] Among them, zinc oxide has recently attracted much attention due to its wide applications to transparent electrodes or wires, UV light emitters, gas sensors, and a window material for displays or solar cells. ZnO is a wide gap n-type semiconductor with a band gap energy of ca. 3.2 eV. Various processes including chemical vapor deposition (CVD), sol–gel, sputtering, vacuum evaporation, laser ablation, thermal plasma, and arc discharge in vacuum conditions have been proposed.[3–5] Accordingly, mass production of ZnO nanoparticles is in high demand.

Plasma processing of materials in liquid has a high potential to be applied to industrial process for mass production of nanosized materials. In recent years, synthesis of nanoparticles such as Au,[6,7] Ag,[8] Cu_2O, CuO,[9] and ZnO[10] by arc or glow discharge in liquids has been investigated. These preparation processes can be largely divided into two categories. In these processes electrons, ions, and radicals, as well as joule heating and UV light, are generated. These species can react at the gas/liquid interface with chemical compounds or ions dissolved in the liquid.[6,7] On the other hand, metal atoms sputtered into liquid by plasma and aggregate to form nanoparticles.[8–10]

Microwaves can be used as the power source of plasma, and smaller plasma equipments can be made with a microwave system according to its high frequency (usually 2.45 GHz).[11] Nomura et al. successfully generated plasma in hydrocarbon liquids and obtained polycrystalline SiC on a Si substrate as well as carbon nanotubes in benzene liquid.[12] But they mentioned that the existence of bubbles in liquid is necessary for generating in-liquid plasma because plasma is apparently generated inside bubbles or around the bubble boundary in the liquid. We have recently reported mass production of metallic gold and silver nanoparticles by microwave induced in aqueous solution of the corresponding metal ions.[13] This plasma in liquid system has some advantages, that is, mass productivity, size uniformity, and low initial and running costs. In this study, we have successfully produced microwave plasma in an aqueous solution of zinc(II) acetate, and rapid production of zinc oxide nanoparticles was achieved at atmospheric pressure.

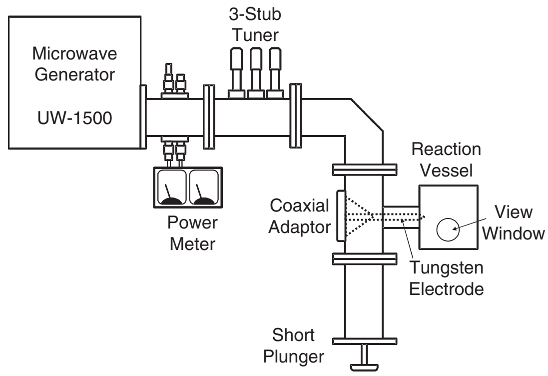

Figure 1. Schematic illustration of a home-made microwave-induced plasma in liquid system.

As a precursor, zinc(II) acetate ($Zn(CH_3COO)_2$, Kanto) was used as received. NaOH was used to adjust pH. Water was purified by an Organo/ELGA purelabo system (>18.2 MΩ). A home-made microwave-induced liquid plasma system was used for the particle preparation as shown in Figure 1. The microwave generator is a UW-1500 (Micro-denshi, Japan) at 2.45 GHz, and the power could be adjusted from 300 W to 1.5 kW. Microwaves emitted from the magnetron pass through a WRJ-2 rectangular wave guide (109.22 × 54.61 mm) and a power meter, a tuner, and a waveguide to the coaxial adaptor. The electrodes were made of tungsten. The tip of the inner electrode of the coaxial line is sharp. The diameter of the aperture of the outer electrode is 5 mm.

TEM images were taken with a Hitachi H-9000 transmission electron microscope with an acceleration voltage of 300 kV. The sample was put on a carbon-coated copper grid. X-ray diffraction pattern was obtained with a Philips X'Pert. Thermo gravimetric measurement was carried out with a Shimadzu DTG-60H with a scan rate of 5 °C min^{-1}.

The preparation procedure was as follows: 1 g of zinc acetate (5.45 mmole) was dissolved into 500 mL of water. Concd aqueous NaOH solution was added to adjust the pH to 11. The solution became a slightly turbid white dispersion with the formation of $Zn(OH)_2$ colloids. No stabilizing reagent was added into this dispersion. The dispersion was then introduced into a Teflon-coated reaction vessel. Gas bubbles, which can assist the plasma ignition, were not injected to the dispersion. Microwave irradiation was maintained for several minutes.

At first, in order to ignite plasma, relatively high power (ca. 1.5 kW) was induced to the electrode. Then, bubbles generated around the electrode and plasma ignited. It is probably due to the joule heating by microwave energy. Many bubbles and light were generated in the electrode area. After ignition, the

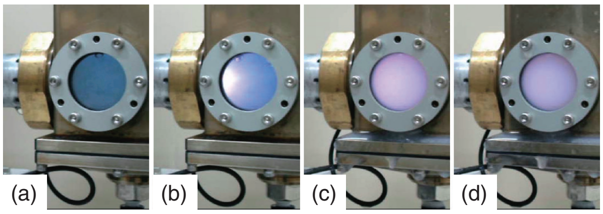

Figure 2. Photographs of the solution during the reaction. (a) Before ignition, (b) plasma ignition, (c) formation of ZnO during plasma irradiation, and (d) ZnO nanoparticles (white).

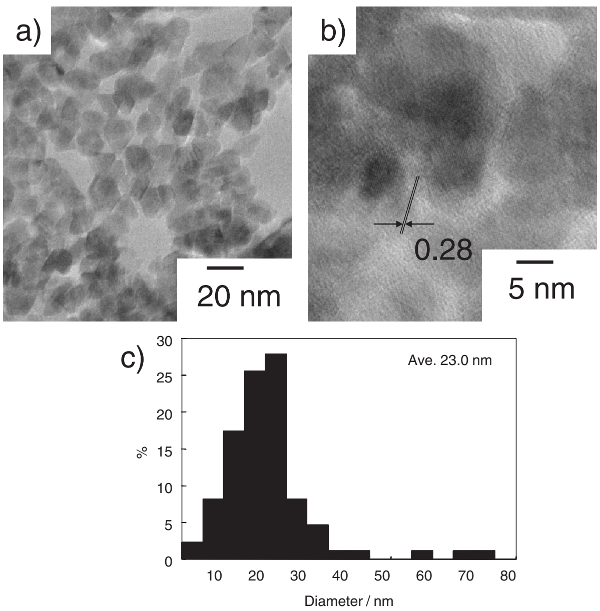

Figure 3. TEM images (a, b) and the size distribution (c) of ZnO nanoparticles prepared by microwave-induced plasma in water from $Zn(CH_3COO)_2$. The gap of the fringe in the high-magnification image (b) corresponds to (100) plane.

microwave power was adjusted at ca. 800 W to obtain continuous and stable plasma. No stirring was applied to this reaction vessel because bubbles well mixed the dispersion.

On the side wall of the reaction vessel, a quartz crystal window was fitted to watch the reaction. In Figure 2, the photographs of the reaction dispersion during the preparation are shown. After ca. 2 min of plasma irradiation, white fine particles appeared around the electrode, and the dispersion instantly turned to white opaque which strongly suggested the formation of zinc oxide particles. The total reaction time used here was ca. 5 min. The obtained powder was collected by filtration over a membrane filter with the pore size of 200 nm (Advantec Toyo). From 1 g of zinc acetate, we could obtain 0.34–0.35 g of zinc oxide; that is, the yield was as high as 77–79%. Considering the short reaction time of this process, microwave-induced plasma in water is a good candidate for mass production of zinc oxide nanoparticles.

The TEM images and the size distribution of the obtained ZnO nanoparticles are shown in Figure 3. The size of the particles is relatively uniform, and the average diameter is 23.0 nm as shown in Figure 3c. The particles clearly show facets, which suggests these particles are crystalline. In the high-resolution TEM image, one can readily find a fringe with the gap of ca. 0.28 nm, which corresponds to (100) surface. An X-ray diffraction pattern of the obtained particles is shown in Figure 4. This pattern clearly shows the crystalline zinc oxide with hexagonal structure. The obtained pattern has sharp peaks at $2\theta = 32.0$, 34.7, 36.5, 47.8, 56.9, 63.0, 66.6, 68.2, 69.4, 72.9, and 77.2° which is in good agreement with the JCPDS card.

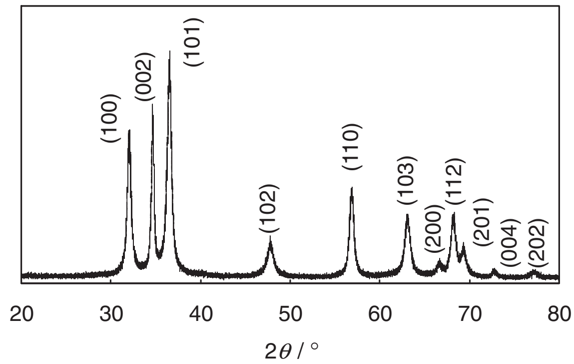

Figure 4. X-ray diffraction pattern of ZnO nanoparticles obtained by microwave-induced plasma.

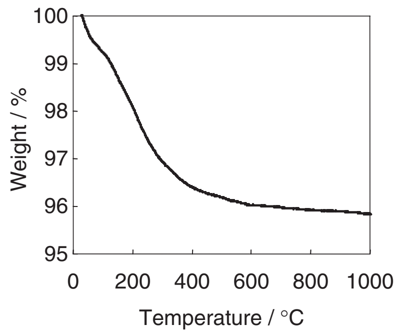

Figure 5. Thermogravimetry curve of ZnO nanoparticles prepared by microwave plasma in water. Scan rate: $5\,°C\,min^{-1}$.

The formation of ZnO in the present case is suggested as the following two processes. One is the simple thermal decomposition of $Zn(OH)_2$. $Zn(OH)_2$ was decomposed at ca. 130 °C to form ZnO.[14] The reaction temperature was not exceeded 100 °C because water was the disperse medium, but around the plasma, the temperature should be much higher. The other process is the reaction with hydroxyl radicals formed by plasma in water. Unfortunately, it cannot be determined which process is dominant in this case.

Thermogravimetric measurement was carried out with a sample which was dried at room temperature under vacuum for overnight. Constant weight loss was observed by the measurement (Figure 5). No significant loss at 130 °C is observed, which suggests these nanoparticles are composed of ZnO, also indicated by an X-ray diffraction pattern (Figure 4).

In summary, zinc oxide crystalline nanoparticles were successfully prepared in one step by microwave-induced plasma irradiation of an aqueous solution of zinc acetate. Investigations on their optical properties and doping are now under due course.

This work is partially supported from Grant-in-Aid for Scientific Research in Priority Area ("Strong Photon–Molecule Coupling Fields (470)") (No. 21020010) from MEXT, Japan and O.S.G. Fund, Japan (to TY). Authors thank Drs. N. Nishida and K. Mori for fruitful discussions and assistances.

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