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Addition of electrical conductivity to metal oxide particles using the polygonal barrel-sputtering method

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ABSTRACT

The surface modification of Al_2O_3 particles with Au was investigated using the polygonal barrel-sputtering method. When the Au was sputtered, a hexagonal barrel loaded with Al_2O_3 particles was oscillated. As a result, the appearance of the sample changed from white to dark brown. The characterization of the prepared sample showed that the surfaces of the Al_2O_3 particles were uniformly modified with Au having a face-centered cubic structure. The electrical conductivity of the prepared sample was very high ($\sigma = 1.19 \times 10^3$–$2.45 \times 10^3$ S m^{-1}) and its electrochemical property was similar to that of the bulk Au metal. Thus, the polygonal barrel-sputtering method is concluded to be useful for providing an electrical conductivity to insulators such as metal oxide particles.

1. Introduction

Metal oxides are chemically stable and are widely used in various scientific and industrial fields. For example, metal oxide particles including SiO_2, Al_2O_3, and ZnO are used as the supports of catalysts for the Fischer–Tropsch reaction [1] and steam reforming reaction [2,3]. TiO_2 is well known to be an important material for photocatalytic reactions [4–6].

The metal oxides are also useful in electrochemical fields such as in batteries. In lithium ion batteries, $LiCoO_2$ and $LiMn_2O_4$ particles are utilized as the cathode [7] and the surface modification of these cathode materials with metal oxides can prevent the lifetime of the lithium ion battery from decreasing [8–10]. Furthermore, it has been reported that the methanol oxidation performances of anode catalysts for direct methanol fuel cells are improved by the addition of TiO_2 [11,12]. However, the metal oxides have a low electrical conductivity, which possibly decreases the power generation of the batteries due to the increase in the overpotential of the electrode reactions.

To address this problem, it is important to impart an electrical conductivity to the electrode particles based on metal oxides by the surface modification with metals. Wet processes, including electroplating [13,14] and impregnation [2,15], are the most widely used methods for particle surface modification. However, wet processes result in wastewater streams which not only require treatment to remove any harmful residual chemicals, but may also be potentially damaging to the environment. In addition, these processes contain a procedure to decompose the precursors, which might lead to the formation of undesirable materials at the interfaces between the particle surfaces and the deposited materials.

Based on this background, we developed a novel surface modification method for powders using a sputtering technique, which we call the "polygonal barrel-sputtering method" [12,16–28]. Since this method is categorized as a dry process, no waste water is discharged during the particle surface modification. In addition, the polygonal barrel-sputtering method uses no precursors, avoiding the formation of interface compounds between the particles and the deposited materials. These advantages can solve the problems of the wet process, as already described. We have already succeeded in the uniform surface modification of particles with metals [16–21], metal alloys [12,22–24], metal oxides [12,25–27], and others [28]. In this study, the surfaces of the

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Al_2O_3 particles were modified with Au using the polygonal barrel-sputtering method to demonstrate the ability to provide an electrical conductivity to metal oxide particles.

2. Experimental

2.1. Preparation of samples

In this study, the particle surface modification was performed using Al_2O_3 powder (AX3-32; Micron). The particle size distribution of the Al_2O_3 powder is shown in Table 1 and the average particle size was 4.6 μm. Before the modification, the Al_2O_3 powder was heated at 180 °C in an oven to prevent particle aggregation by the water during the preparation. An Au plate (purity: 99.99%) with a size of W 50 mm × L 100 mm was used as the target for sputtering and the AC power for the sputtering was supplied by RF power generation (13.56 MHz) [16–21]. The sample was prepared following reported procedures [12,16–28]. A 10-g Al_2O_3 powder sample (sample volume: 17 cm^3) was introduced into a hexagonal barrel (sample-filling height on the barrel: less than 2 mm) and then the barrel was placed in a vacuum chamber. Subsequently, the vacuum chamber was carefully evacuated using rotary and diffusion pumps. After the pressure was decreased to less than 8×10^{-4} Pa, Ar gas (purity: 99.9999%) was slowly introduced into the chamber. Sputtering was then performed at an Ar gas pressure of 2 Pa without heating while the hexagonal barrel was oscillated at intervals of 14 s and amplitude of ±75° to stir the Al_2O_3 particles. The distance between the Au target and the stirred Al_2O_3 particles on the barrel was *ca.* 50 mm. The AC power and sputtering time were 195 W and 3.5 h, respectively. After the sputtering, N_2 gas was gradually introduced into the vacuum chamber until it reached atmospheric pressure, at which point the prepared sample could be extracted.

2.2. Characterization of sample

The Al_2O_3 powder samples before and after the sputtering were observed using a field emission scanning electron microscope (FE-SEM; JSM-6701F; JEOL) with an energy-dispersive X-ray spectroscope (EDS; JED-2300; JEOL). To measure an amount of Au deposited on the Al_2O_3 particles, the prepared sample of 10 mg was stirred at room temperature for 6 h in an aqua regia. After the obtained solution was diluted with ultrapure water, the Au concentration was determined by atomic absorption spectrometry (contrAA700; Analytik Jena). The prepared sample was also characterized by X-ray diffraction (XRD; PW1825/00; Philips) with Cu Kα radiation.

2.3. Evaluation of electrical conductivity of sample

The electrical conductivity of the Al_2O_3 particles after the sputtering with Au was measured using two kinds of glass tubes with sizes of ϕ1.2-mm inner diameter × 5.5-mm length and ϕ0.3-mm inner diameter × 10-mm length. The prepared powder sample was tightly pushed into these glass tubes using an Au wire to prevent the packed sample from moving during the measurements. Then, tungsten probes (tip diameter: 42 μm) were mechanically contacted to both sides of the sample using a chamber system for the microconductivty measurement (LMT-S-700; Collet Kogyo). After the probes were connected to a system source meter (2612A; Keithley Instruments), the current–voltage characteristic was measured at the sweep rate of 100 μV s^{-1} in the voltage range of −2 and +2 mV. This measurement was conducted more three times by repacking the sample into the glass tubes. From the obtained resistance (R in Ω), the electrical conductivity of the sample (σ in S m^{-1}) was determined using the following equation:

$$\sigma = 1/\rho = L/RS, \quad (1)$$

where ρ is the volume resistivity (Ω m), and L and S are the length (in m) and the cross-sectional area (in m^2) of the glass tube including the sample, respectively.

The effectiveness of the surface modification with Au on the electrical conductivity of the Al_2O_3 particles was also electrochemically investigated by cyclic voltammetry using an Ag/Ag_2SO_4 electrode [29,30] and a Pt wire as the reference and counter electrodes. A porous microelectrode (PME) used as the working electrode was prepared as follows [31–33]. A ϕ50 μm Au wire was inserted into a glass capillary and heat-sealed by decompressing the air inside the glass. By using lapping films, the tip of the capillary was then polished. Subsequently, the tip of the Au electrode was etched at a current density of 0.1 A cm^{-2} for 300 s in a 1 mol dm^{-3} HCl aqueous solution, resulting in the formation of a cavity with a depth of 20 μm. The powder sample was then packed into this cavity. Using this working electrode, the potential cycling was conducted at the sweep rate of 10 mV s^{-1} between 0.075 and 1.8 V vs. RHE for 45 min in a N_2-saturated 0.5 mol dm^{-3} H_2SO_4 solution which was prepared by diluting conc. H_2SO_4 (Wako Pure Chemical Industry) with Milli-Q water, so that the stable cyclic voltammogram was obtained.

Table 1
Particle size distribution of Al_2O_3 powder.[a]

Particle size/μm	Distribution/%
<2	23.0
2–4	20.6
4–6	19.4
6–8	14.0
8–12	13.0
12–16	5.4
16–24	3.8
24–32	0.8

[a] Data were provided by Micron.

3. Results and discussion

3.1. Characterization of the Al_2O_3 sample modified with Au

Fig. 1(A) shows photographs of the Al_2O_3 samples (I) before and (II) after the sputtering with Au. The white Al_2O_3 powder changes to dark brown in color after the sputtering. Fig. 1(B) and (C) represent the SEM images and EDS mapping images of (I) the

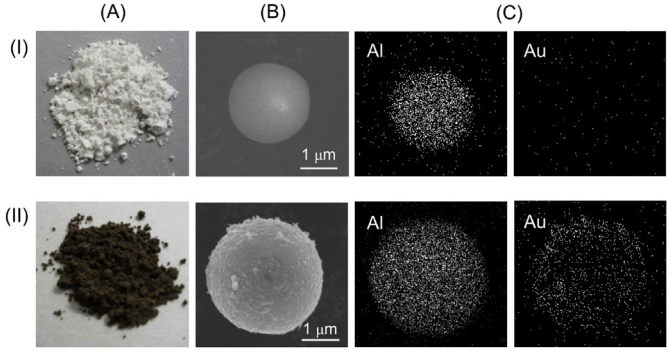

Fig. 1. (A) photographs, (B) FE-SEM images, and (C) EDS mapping images of Al_2O_3 particles (I) before and (II) after the sputtering with Au.