

## Electronic Supplementary Material

### Composites of SnO<sub>2</sub>/layered SnO<sub>x</sub> compounds and their electrical properties

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#### 1. Experimental procedure

##### 1.1 Materials

Stannous chloride (97%), polyvinyl alcohol (completely hydrolysed, average polymerization degree: 400–600), sodium hydroxide (97%), and hydrogen peroxide solution (30wt%) were purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used without further purification.

##### 1.2 Synthesis of composites of SnO<sub>2</sub> crystal and layered SnO<sub>x</sub> compounds

Stannous chloride (12.9 g) and polyvinyl alcohol (5.00 g) were dissolved in deionized water (482 g) and poured into a 1 L glass round-bottomed flask. After the solution temperature was elevated 90 °C, 0.95 wt% sodium hydroxide aqueous solution was slowly added dropwise into the raw material solution and stirred with a 35 nm diameter paddle until the pH value reached 4.3. Next, 6 wt% hydrogen peroxide solution was slowly added dropwise to the obtained slurry in an amount equimolar with the Sn content. The slurry then stood for 10 minutes so the reaction could complete. The obtained precipitates were repeatedly washed by decantation and redispersion in deionized water until the conductivity of the supernatant became less than 100 μS•cm<sup>-1</sup>. The slurry obtained after this washing procedure was filtered under a reduced pressure and dried in air at 120–400°C for 3 hours. To obtain samples for characterization, the product was finely ground using a mortar and pestle and sorted through a SUS mesh with a 75 μm aperture.

## 2. Characterization

The crystal structure of the powder was identified by performing X-ray diffraction (XRD) analysis, where the data were calibrated using an external Si standard. Powder samples were filled in a dedicated glass holder. Measurements were performed on a diffractometer (Rigaku RINT-TTR III) with Cu K $\alpha$  radiation. The operating power was 50 kV at 300 mA. The fixed time (FT) method was used with a step angle of 0.01° and a step time of 1 sec. The peak positions (2 $\theta$ ) were identified using the peak top method after the background was removed and the K $\alpha$ 1 and K $\alpha$ 2 components were separated in the obtained measurement data. The spacing distance  $d$  (Å) was calculated from the peak positions using Bragg's equation.

The constituent elements of the synthesized particles were first qualitatively analysed by performing dissolution in HCl solution and then using inductively coupled plasma (ICP) (SII SPS-3500DD). Next, quantitative analysis was carried out on the detected elements. Quantitative analysis for C and Cl, the constituents of the raw materials that cannot be characterized by ICP, was conducted as follows. The sample was heated and oxidized in flowing oxygen using gas analysis equipment (Horiba EMIA-920V) to convert C to carbon dioxide and carbon monoxide, and the carbon content in the gases was quantified using an infrared detector. The chloride ion content was measured by adding silver nitrate to nitric acid solutions of the powder to precipitate silver chloride and then performing turbidimetry to assess the resulting mixtures.

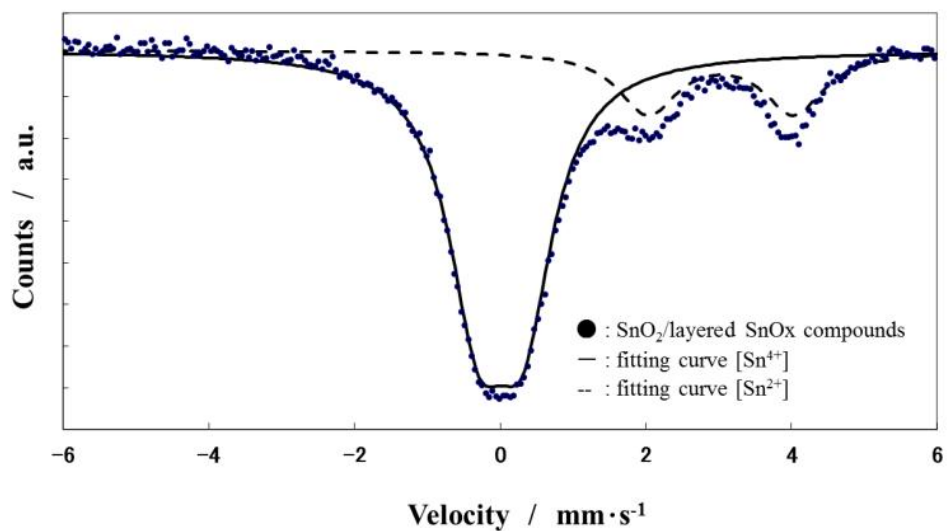
The morphology of the particles was observed using field emission transmission electron microscopy (FE-TEM, JEOL JEM-ARM200F). The powder samples were prepared by microsampling using a focused ion beam (FIB, Hitachi FB-2100A). First, the samples were cut out into blocks with sides of a few  $\mu$ m and thicknesses of about 100 nm. Then, the blocks were thinned to a thickness of ~40 nm by ion milling (FISCHIONE MODEL-1010) and observed using FE-TEM.

The valence of Sn in the SnO<sub>2</sub>/layered SnO<sub>x</sub> compounds measured by <sup>119</sup>Sn transmission Mössbauer spectroscopy (TMS). The TMS spectra of SnO<sub>2</sub>/layered SnO<sub>x</sub> compounds were measured at room temperature under ordinary pressure where <sup>119m</sup>Sn/CaSnO<sub>3</sub> was used as the 23.8 keV  $\gamma$ -ray source. The velocity was calibrated using <sup>57</sup>Fe source and Fe foil as an absorber. The spectra were fitted to Lorentzian curves by the non-linear least squares method. Composition ratio of Sn<sup>2+</sup> and Sn<sup>4+</sup> was calculated by relative area ratio of spectra.

The specific electrical resistance of the synthesized SnO<sub>x</sub> compound powders was measured using the four-point probe method under a load of 500 kg/cm<sup>2</sup> after filling 1.00 g of powder in a 20-mm-diameter cylinder (Mitsubishi MCP-PD51).

**Table S1.** Spacing distances  $d$  obtained from the unknown XRD peaks

| $2\theta$<br>(deg./CuK $\alpha$ ) | $d$<br>(Å) |
|-----------------------------------|------------|
| 9.370                             | 9.430      |
| 18.800                            | 4.716      |
| 28.340                            | 3.146      |
| 48.150                            | 1.888      |
| 58.600                            | 1.574      |



**Figure S1.** Mössbauer spectra of SnO<sub>2</sub>/layered SnO<sub>x</sub> compounds