Supplementary Information to:

Reduction Behaviors of Tin Oxides and Hydroxides Itself during Electrochemical Reduction of Carbon Dioxide in an Aqueous Solution under Neutral Conditions

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CONTENTS

Appendix Experimental Section

Preparation of a metallic Sn electrode. A metallic Sn electrode was prepared by an electrodeposition method. A specimen used for electrodeposition comprised 99.5% pure titanium sheets of 0.5 mm thickness. The specimen was electropolished in 1 mol dm^{-3} NaCl/ethylene glycol solution at 293 K at 20 V for 200 s and, subsequently, at 10 V for 600 s. Electrodeposition was carried out using a normal three-electrode system with a commercial potentiostat and potential programmer (Toho Technical Research Co., Ltd., Model PS-04). A platinum foil (1.5 × 1.5 cm^2) and Ag/AgCl/KCl (satd.) were used as counter and reference electrodes, respectively. The electropolished specimen was immersed in 5 mmol dm^{-3} $SnCl_2$ aqueous solution, then, applied potential at -1.2 V vs. RHE for 30 min. The lateral and back sides of the obtained Sn/Ti electrode was covered with epoxy resin for insulation (effective area is 1.0×1.0 cm^2).

Synthesis of SnO_2 ultrasmall particles. SnO_2 ultrasmall particles loaded on acetylene black nanoparticles were prepared by a reverse micelles deposition (RMD)[1] and following solvothermal method. $SnCl_2 \cdot 2H_2O$ (Fujifilm Wako Pure Chemical Corp. 97.0%) was used as starting materials. 1.0 cm^3 of $SnCl_2$ aqueous solution was stirred with cyclohexane (18.0 g, FUJIFILM Wako Pure Chemical Corp., 99.5%) and hexaethyleneglycol nonyl phenyl ether (9.0 g, NP-6, DKS Co. Ltd.) as a surfactant at 283 K for 30 min to obtain a RM solution containing metal cations (RM-A). Another RM solution (RM-B) was also prepared from cyclohexane (54.0 g), NP-6 (27.0 g) and 10% tetramethylammonium hydroxide (TMAH) aqueous solution (3.0 cm^3 g, KISHIDA CHEMICAL Co. Ltd.). The molar ratios of water to surfactant and cyclohexane to surfactant in the all RM solutions were 3, respectively. RM-A and RM-B were mixed and agitated at 283 K for 1 h, then stirred again by ultra-sonication, and the thus obtained final solution was named as RM-AB. acetylene carbon black powder (AB, 41 mg, STREM Chemicals, Inc.) dispersed in 100 cm^3 of cyclohexane and 200 cm_3 of ethanol were added into RM-AB and the suspension was mixed by a magnetic stirrer at 550 rpm for 1 h. Finally, the formed solid was collected by centrifugation at 10000 rpm, dried at 383 K for overnight in air. The obtained powders were dispersed mixed solution of ion-exchanged water and propylene glycol (Fujifilm Wako Pure Chemical Corp. 99.0%) (1 : 1 volume ratio). The suspension was put into a batch autoclave reactor and heated at 433 K for 3 h without stirring. After reaction, the suspension was cooled with water, and the solid was collected by centrifugation at 4000 rpm and dried at 383 K for overnight.

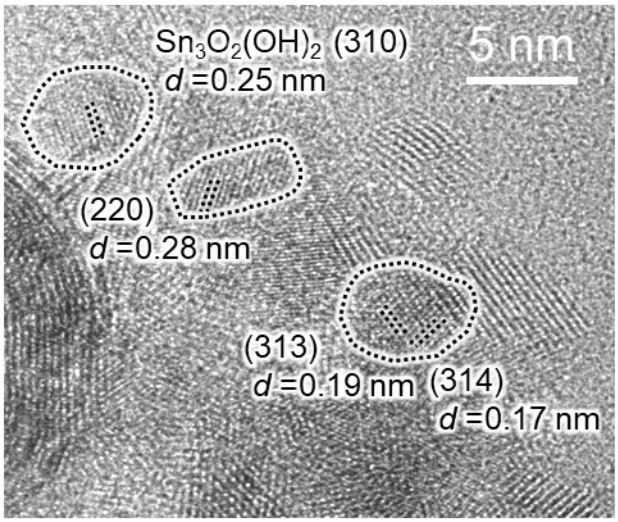

Figure S1 the high-resolution TEM image of P-SNO before constant potential measurements at -0.8 V vs. RHE in CO_2 saturated $NaHCO_3$ aqueous solution.

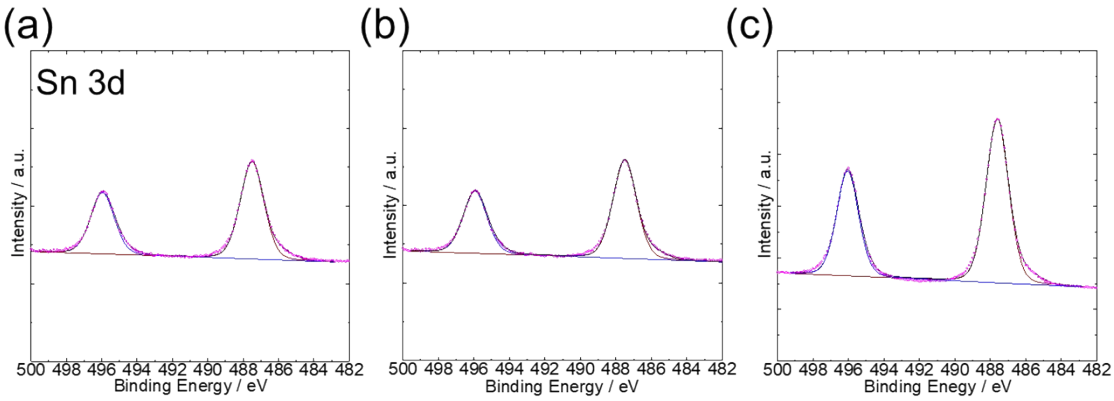

Figure S2 XPS spectra of Sn3d of (a) ST-SNO, (b) SG-SNO and (c) P-SNO/carbon paper electrodes before constant potential measurements at -0.8 V vs. RHE in CO_2 saturated $NaHCO_3$ aqueous solution.

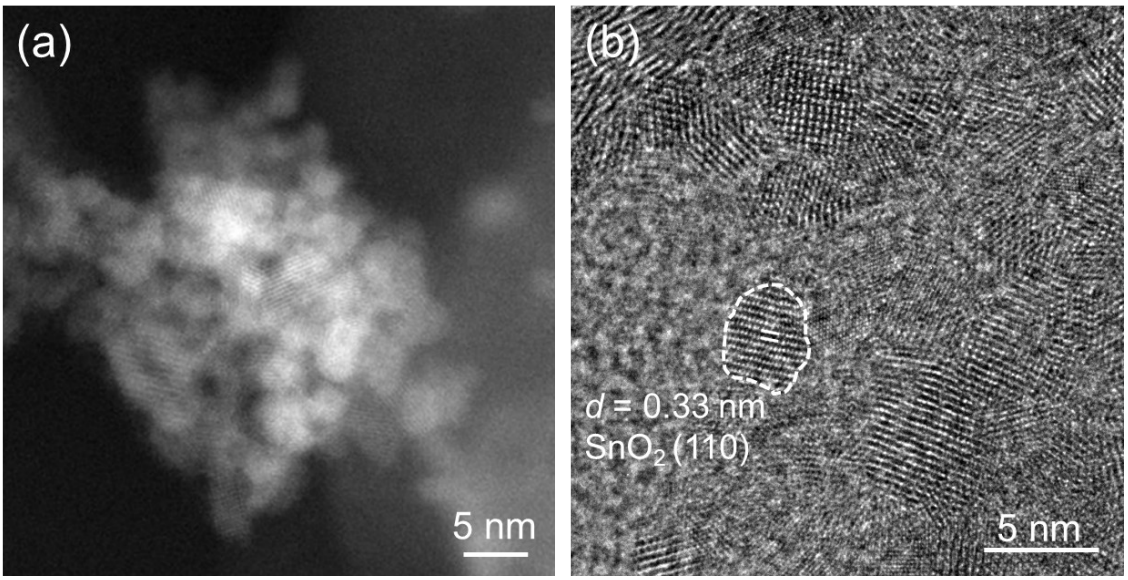

Figure S3 (a) STEM and (b) high-resolution TEM images of SnO_2 ultrasmall particles synthesized on acetylene black by the RMD and solvothermal method. Particle size is less than 5 nm.

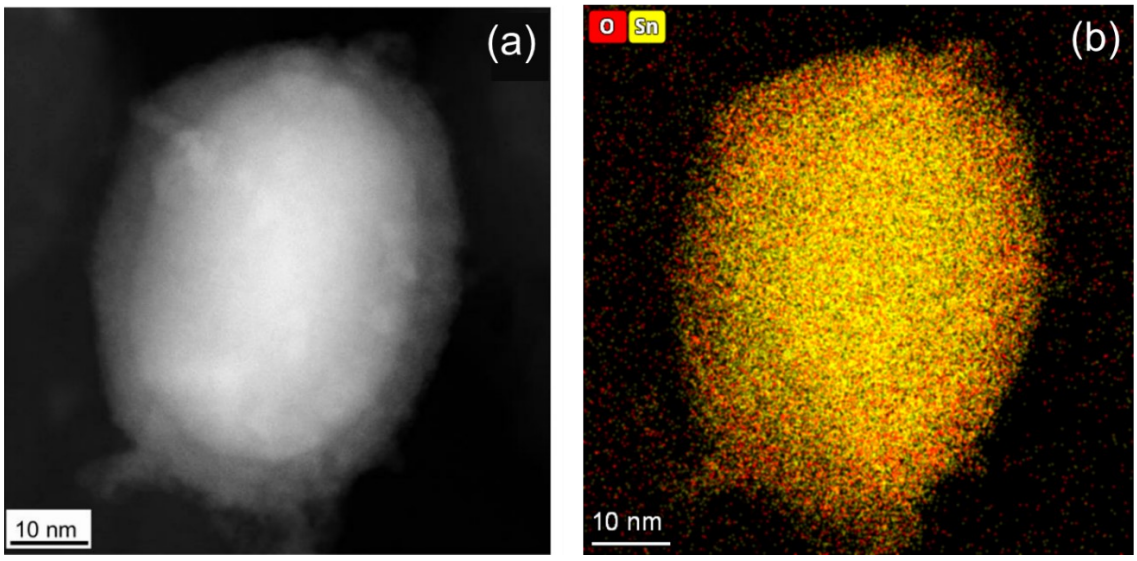

Figure S4 (a) STEM and (b) EDS mapping of reduced nanoparticles, which was formed by reduction of SnO_2 ultrasmall particles during CO_2RR at -0.8 V vs. RHE. The particle is core-shell structures, and particle size is about 40 ~ 50 nm. The particles were quite similar to that formed by reduction of SnO_2 nanoparticles and the tin oxyhydroxide containing amorphous phase and crystalline $Sn_3O_2(OH)_2$ shown in the main manuscript.