

Supporting Information

Pt₂SnCu nanoalloy with surface enrichment of Pt defects and SnO₂ for efficient electrooxidation of ethanol

Meihua Huang,^{a,b} Wangliang Wu,^{a,b} Chuxin Wu,^{a,b} and Lunhui Guan ^{*a,b}

*^a Key Laboratory of Design and Assembly of Functional Nanostructures,
Fujian Institute of Research on the Structure of Matter, Chinese Academy
of Sciences, Fuzhou, 350002, China.*

*^b Fujian Provincial Key Laboratory of Nanomaterials, Fujian Institute of
Research on the Structure of Matter, Chinese Academy of Sciences,
Fuzhou, 350002, China.*

Experimental

*Preparation of carbon supported Pt₂SnCu nanoalloy with surface riched
SnO₂ clusters and Pt defects.*

In a typical synthesis, Cu(CH₃COO)₂·H₂O, SnCl₄·5H₂O, H₂PtCl₆ solution (0.019097544 mmol mL⁻¹) and Vulcan XC-72R carbon were mixed with 140 ml ethylene glycol (EG) in a 250 mL beaker. The atomic ratios of Pt, Sn and Cu are 2:1:1. After about 30 min of ultrasonic treatment to form uniform carbon ink, the pH value of the ink was adjusted to about 8 by adding 0.1 mol L⁻¹ NaOH-EG solution. The ink was treated in an ultrasound bath for another 30 min. Then the beaker was placed the center of a microwave oven (2450 MHz, 1000 W) and nitrogen

gas was feed into the ink for 30 min to remove oxygen. The ink was heated up to boiling point by microwave and refluxed for 7 min so that the Pt^{4+} , Sn^{4+} and Cu^{2+} ions were reduced completely. The ink was allowed to cool down to room temperature with continuous stirring, and then the ink was filtered with ultrapure water and ethanol. The filter cake was dried in a vacuum oven at room temperature for 10 h and the obtained sample is denoted as “ $\text{Pt}_2\text{SnCu/C}$ ”. Then the $\text{Pt}_2\text{SnCu/C}$ was ground and heated in air at 200 °C for 60 min. The heated sample is denoted “ $\text{Pt}_2\text{SnCu-O/C}$ ”. Approximately 60 mL of 0.5 M H_2SO_4 solution was mixed with the $\text{Pt}_2\text{SnCu-O/C}$ and the mixture was kept for 2 days. Finally the mixture was filtered and washed by ultrapure water. The filter cake was dried in a vacuum oven at room temperature for 10 h and the obtained sample is denoted as “ $\text{Pt}_2\text{SnCu-O-A/C}$ ”. For comparison, PtSn/C and PtSn-O/C are prepared by the same method. For avoiding Pt_2SnCu nanoparticles aggregation in the process of heating and characterizing Pt_2SnCu hybrid nanostructures clearly, the Pt weight ratio in $\text{Pt}_2\text{SnCu/C}$ was 8.8 wt % in theory. All chemicals are used as received without further purification. Ultrapure water (18.3 M Ω) was used for all solution preparations.

Materials Characterization.

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer (Rigaku D/max-2500 X-ray generator, Cu $K\alpha$

radiation) to study the crystallographic information of samples. The morphology of samples were further studied by transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) and scanning transmission electron microscopy (STEM; FEI Titan 200, 200 kV). The near surface composition and surface electronic information of the synthesized samples were investigated by X-ray photoelectron spectroscopy (XPS). Inductively coupled plasma emission spectroscopy (ICP) results show that the Pt wt% values for the Pt₂SnCu/C, Pt₂SnCu-O/C and Pt₂SnCu-O-A/C are 8.41, 8.96 and 9.26%, respectively.

Electrochemical Measurements.

The electrochemical activities of the synthesized nanocatalysts and commercial Pt (20 wt %; Johnson Matthey) were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The measurements were performed using a three-electrode cell with a CHI660C electrochemical workstation at 26 ± 0.2 °C. A piece of Pt foil was used as the counter electrode. Mercury sulfate electrode (MMS) was used as the reference one. Typically, the catalyst dispersion was prepared by mixing 2.5 mg of catalyst, 2.0 mL of ethanol and 30 μ L of 5 wt % Nafion solution, followed by ultrasonication for 10 min. Then the glassy carbon electrode was polished and rinsed ultrasonically with ultrapure water. Finally, the catalyst slurry was spread on the glassy carbon electrode using syringe, and it was used as the working electrode. Ethanol

oxidation experiments were carried out in 0.5 M H₂SO₄ + 1.0 M CH₃CH₂OH with a scan rate of 50 mV s⁻¹. Due to slight contamination, the working electrode was cycled at 50 mV s⁻¹ until stable cyclic voltammograms were obtained in the 0.5 M H₂SO₄ solution. Before the experiments, all electrolyte solution was purged with ultrapure N₂ gas for 30 min to expel oxygen.

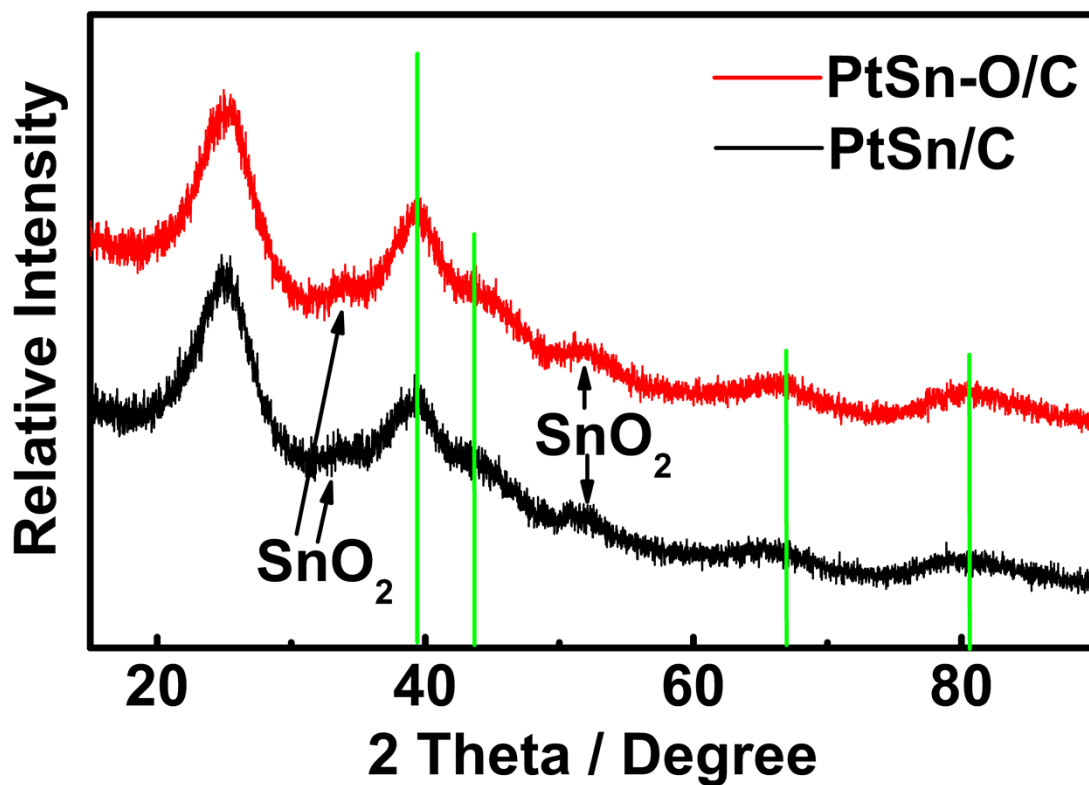


Figure S1. XRD patterns of the synthesized samples.

For comparison, the XRD patterns of the PtSn/C and PtSn-O/C are presented in Figure S1. Seeing from Figure S1, the Pt (FCC) structure of the PtSn/C and PtSn-O/C is the same. By in-situ surface oxidation, the intensity of SnO₂ of the PtSn-O/C at about $2\theta = 34.5^\circ$ and 52.0° is increased. Meanwhile, the the peaks of SnO₂ in the PtSn/C are also observed at about $2\theta = 34.5^\circ$ and 52.0° , which show that the surface Sn atoms are easily oxidized. The results are in agreement with the literatures and show that our experimental design of *in-situ* surface oxidation is feasible.¹

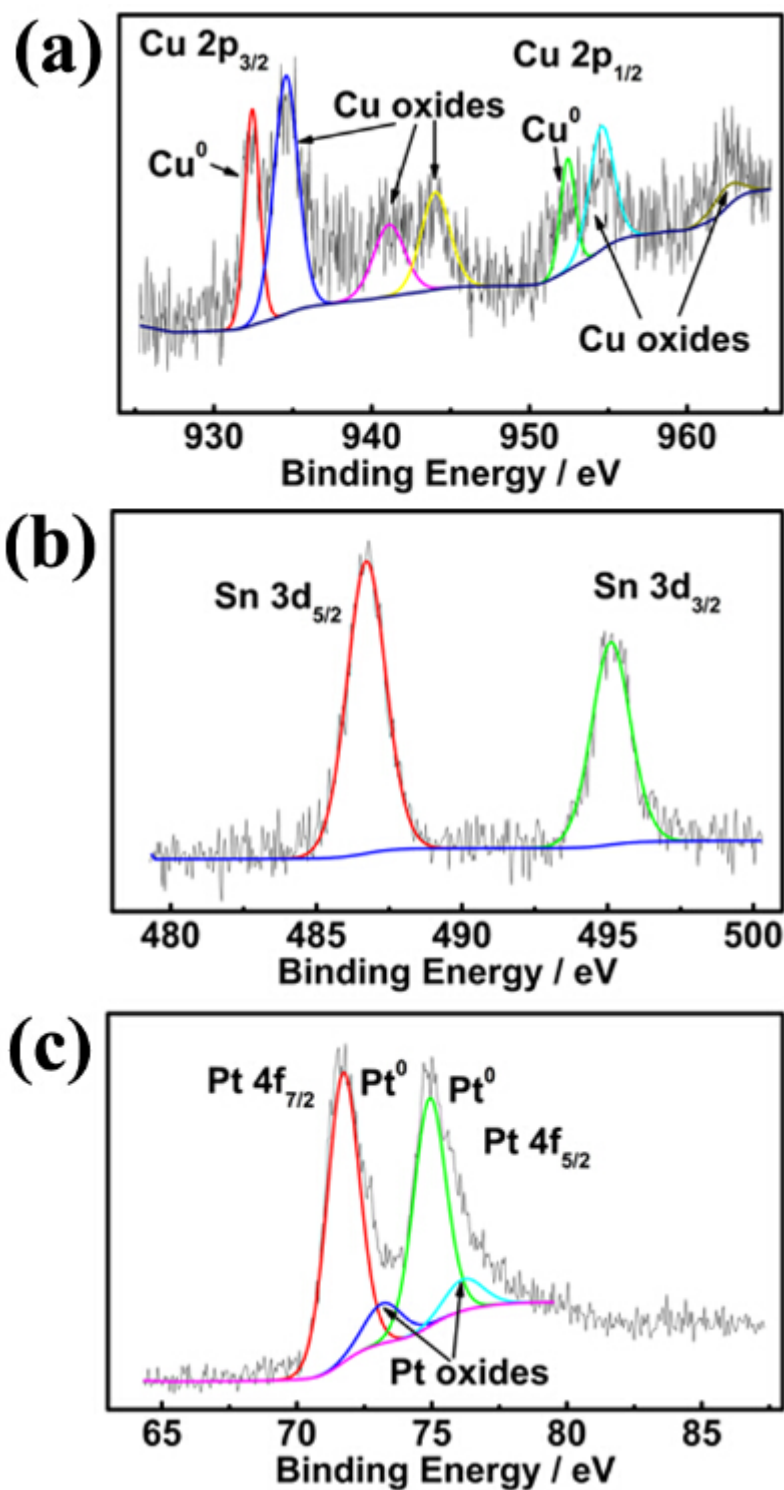


Figure S2. Core level XPS profiles of (a) Cu 2p region for the Pt₂SnCu/C. (b) Sn 3d region for the Pt₂SnCu/C. (c) Pt 4f region the Pt₂SnCu/C.

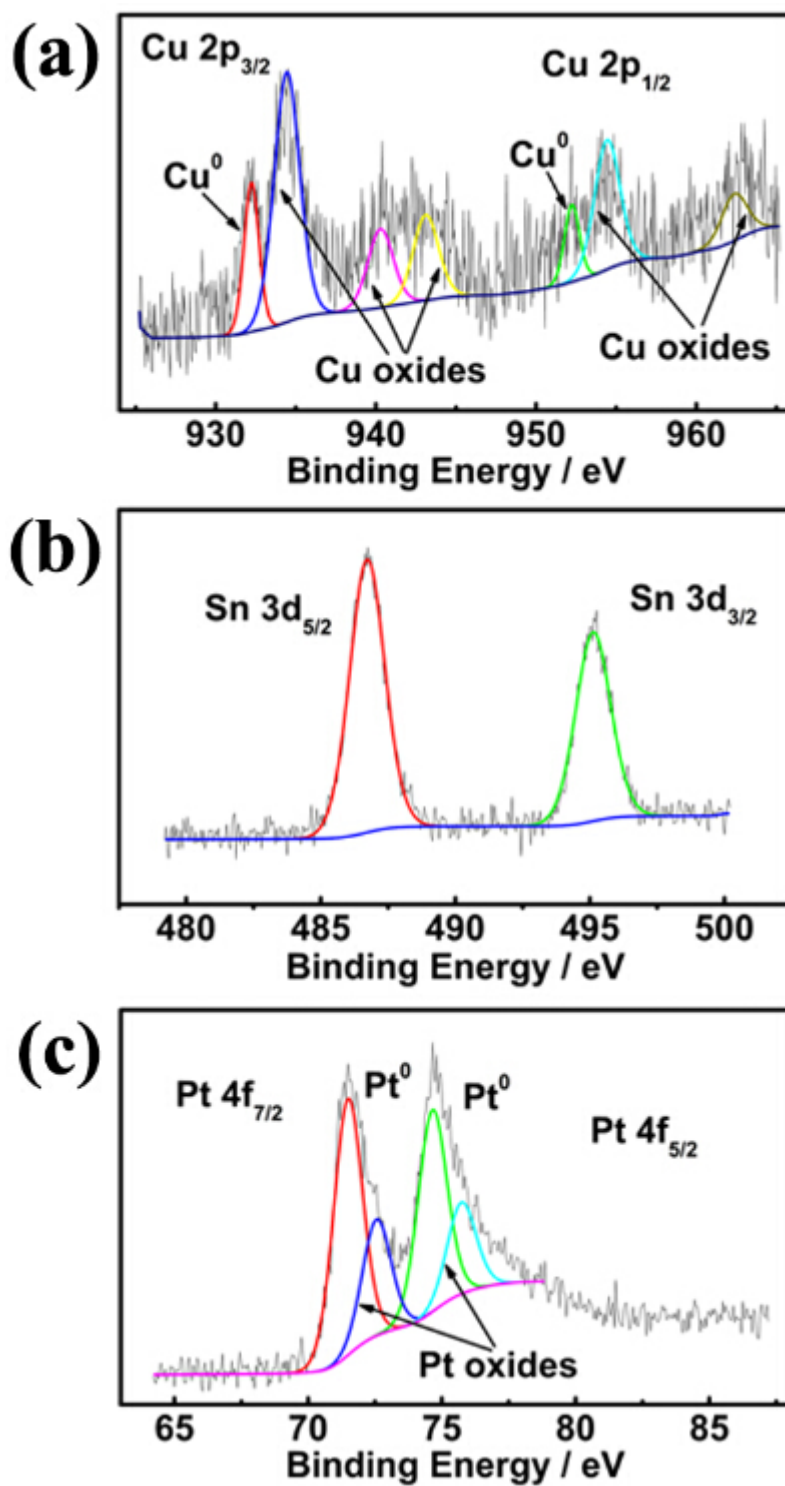


Figure S3. Core level XPS profiles of (a) Cu 2p region for the Pt₂SnCu-O/C. (b) Sn 3d region for the Pt₂SnCu-O/C. (c) Pt 4f region the Pt₂SnCu-O/C.

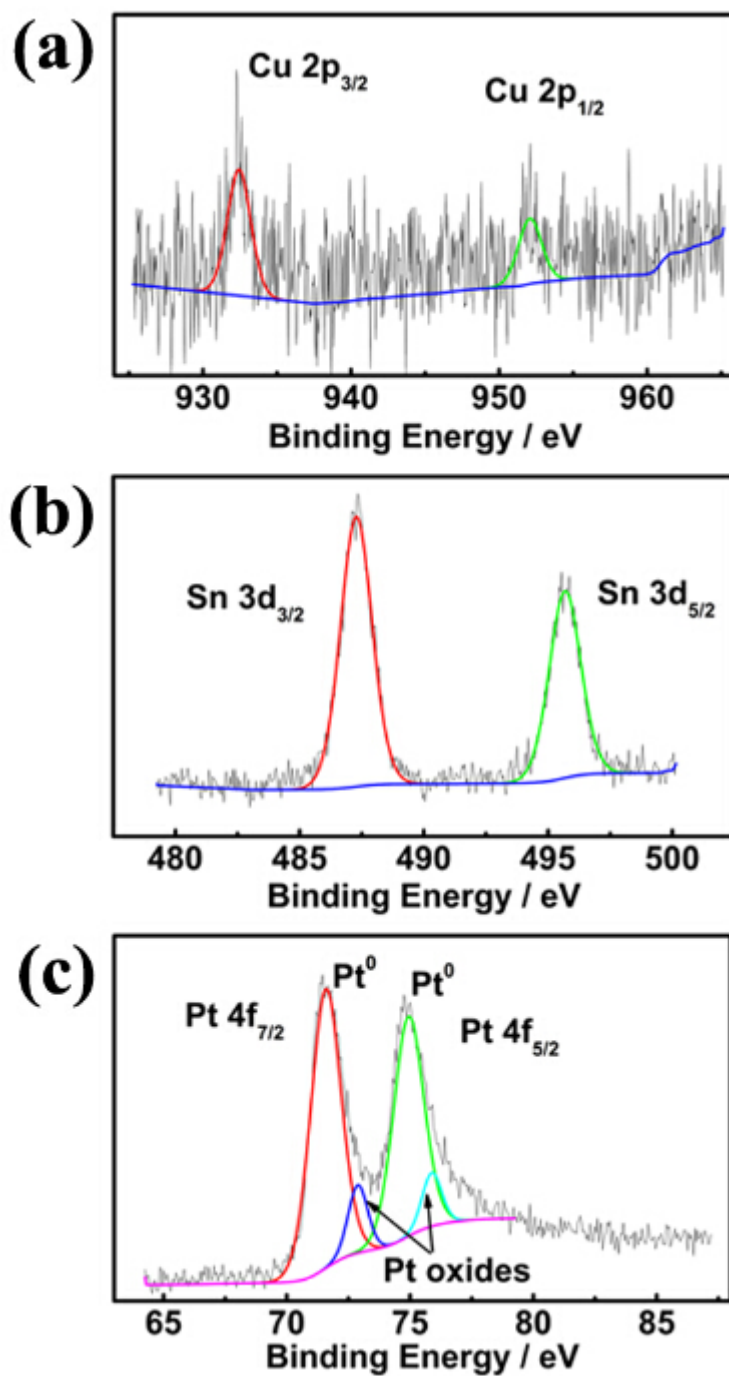


Figure S4. Core level XPS profiles of (a) Cu 2p region for the Pt₂SnCu-O-A/C. (b) Sn 3d region for the Pt₂SnCu-O-A/C. (c) Pt 4f region the Pt₂SnCu-O-A/C.

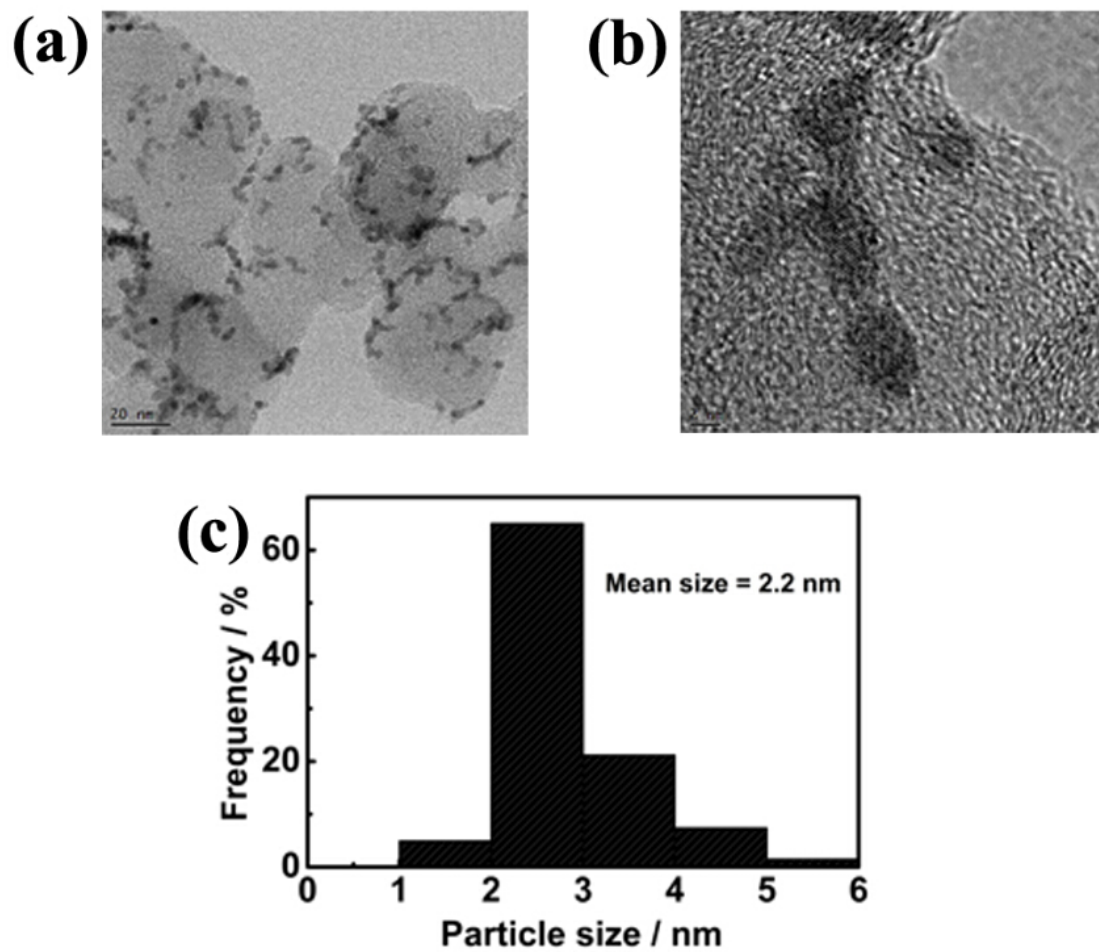


Figure S5. (a) and (b) TEM and HRTEM micrograph of the $\text{Pt}_2\text{SnCu/C}$.
(c) Histogram of particle size distribution of the $\text{Pt}_2\text{SnCu/C}$.

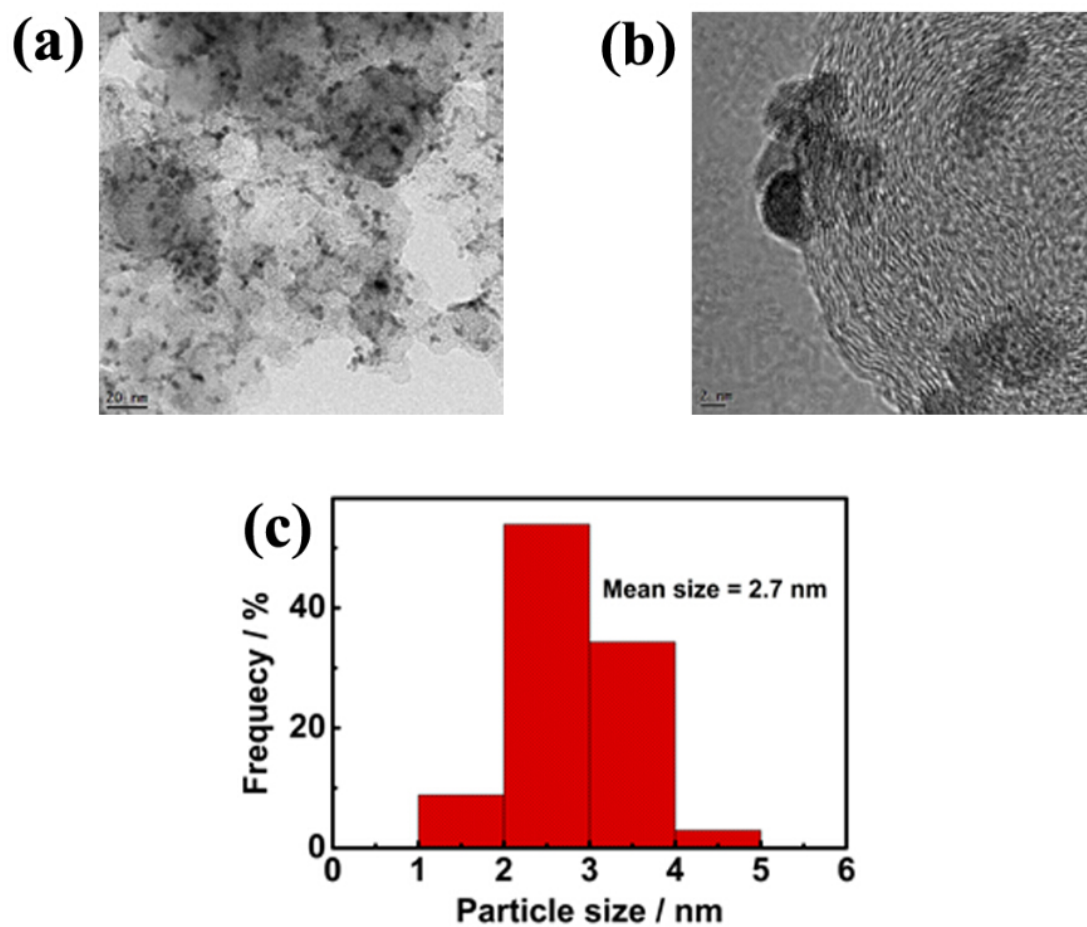


Figure S6. (a) TEM and HRTEM micrograph of the $\text{Pt}_2\text{SnCu-O/C}$. (c) Histogram of particle size distribution of the $\text{Pt}_2\text{SnCu-O/C}$.

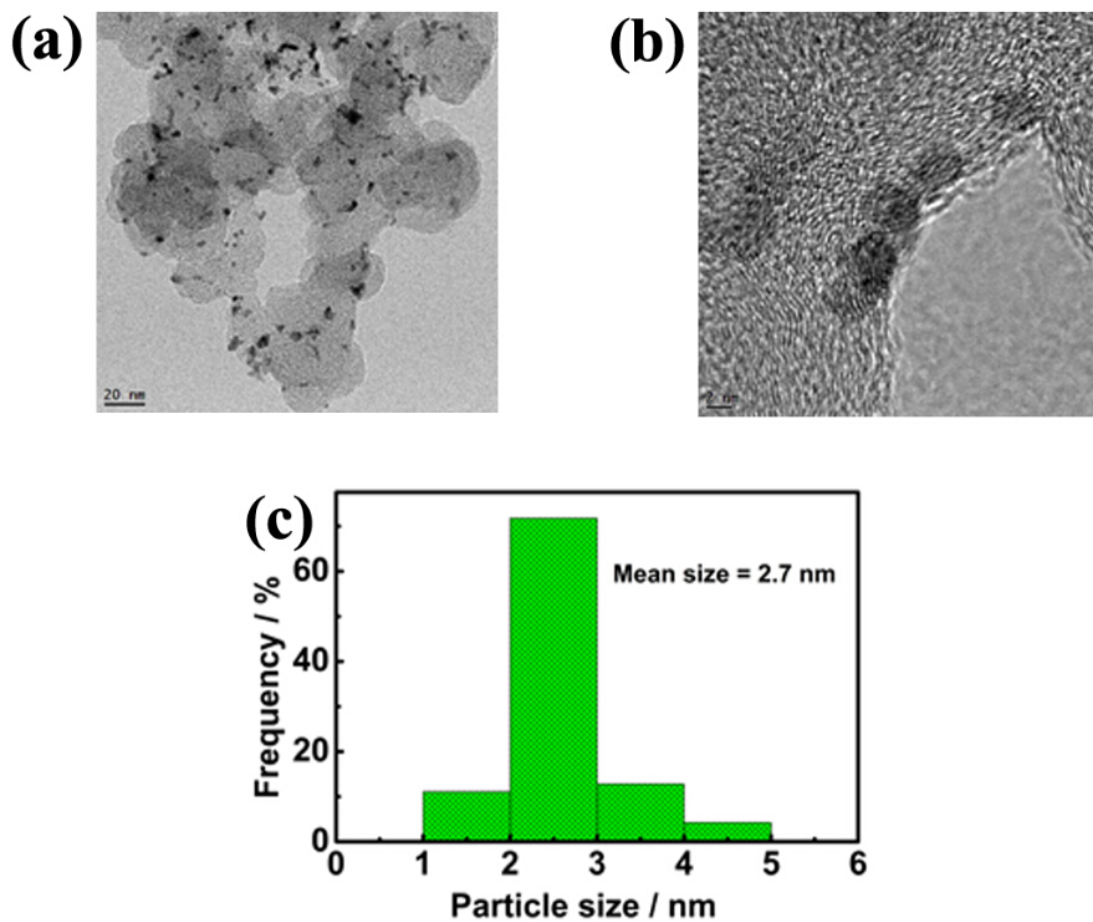


Figure S7. (a) and (b) TEM and HRTEM micrograph of the $\text{Pt}_2\text{SnCu-O-A/C}$. (c) Histogram of particle size distribution of the $\text{Pt}_2\text{SnCu-O-A/C}$.

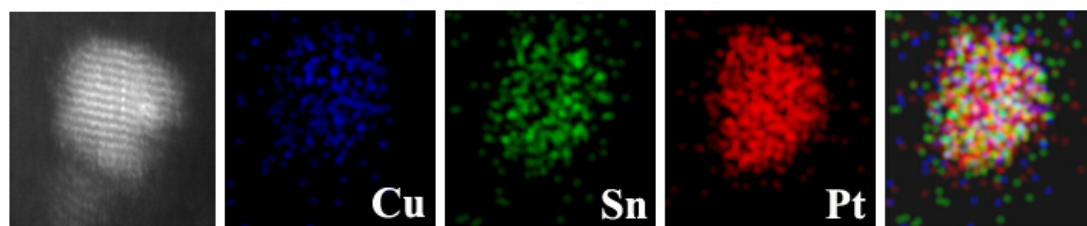


Figure S8. STEM image and elemental scanning images of the $\text{Pt}_2\text{SnCu-O-A/C}$.

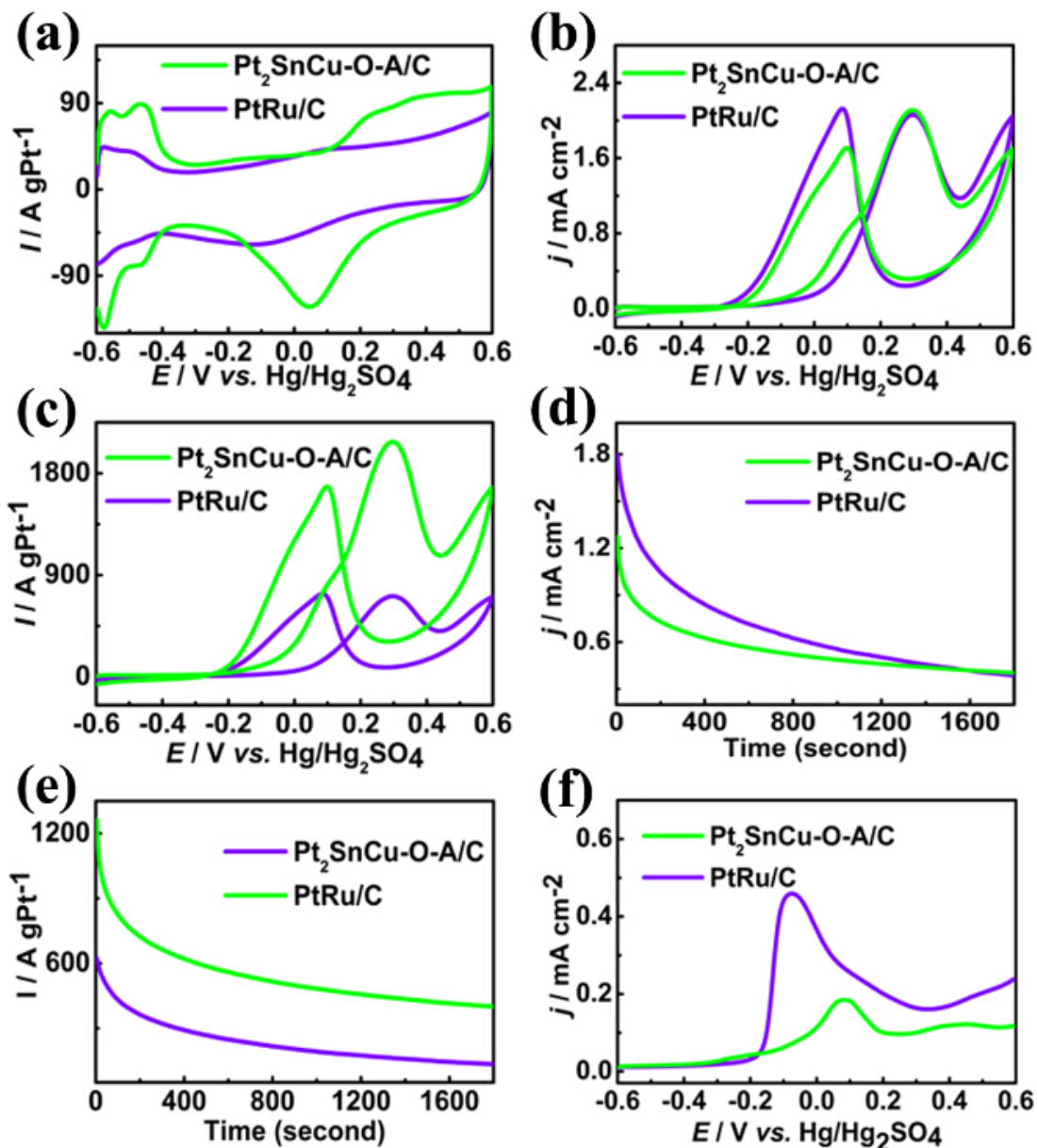


Figure S9. (a) CVs on the Pt₂SnCu-O-A/C and PtRu/C at 50 mV s⁻¹ in 0.5 M H₂SO₄ at 26 °C. (b) and (c) Specific activity and mass activity of the Pt₂SnCu-O-A/C and PtRu/C at 50 mV s⁻¹ in 1.0 M C₂H₅OH + 0.5 M H₂SO₄ at 26 °C. (d) and (e) Current–time curves of the Pt₂SnCu-O-A/C and PtRu/C at 0.2 V in 1.0 M C₂H₅OH + 0.5 M H₂SO₄ at 26 °C. (f) CO stripping voltammograms of the Pt₂SnCu-O-A/C and PtRu/C at 50 mV s⁻¹ in 0.5 M H₂SO₄.

Commercial PtRu/C is also investigated to examine ethanol and CO oxidation. The results are presented in Figure S9. The forward peak surface activity measured for the Pt₂SnCu-O-A/C and PtRu/C are basically the same, but the onset potential of the Pt₂SnCu-O-A/C is lower than that of the PtRu/C. The peak mass activity of the Pt₂SnCu-O-A/C is 2078.1 A g⁻¹, 2.9 times greater than that of the PtRu/C. Figure S8a-S8b show the current-versus-time curves recorded at 0.2 V for 1800 sec. It is found that the end-point current density obtained from the Pt₂SnCu-O-A/C is higher than those of the PtRu/C. During the CO oxidation, the onset potentials of the Pt₂SnCu-O-A/C and PtRu/C for CO oxidation are -400 and -215 mV, respectively. Therefore, the Pt₂SnCu-O-A/C also exhibits enhanced electrocatalytic activity for ethanol oxidation compared with PtRu/C.

References

- (1) R. Crisafulli, R. M. Antoniassi, A. O. Neto, E. V. Spinacé, *Int. J. Hydrogen Energy*, 2014, **37**, 5671.