

Supporting Information

Carbon-Free Electrocatalyst for Oxygen Reduction and Oxygen Evolution Reactions

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Fabrication of nanoporous Ag-doped SnO₂ thin-film

Commercial copper foils (25 μm , 99.8%, Alfa-Aesar) were electropolished in a polishing solution comprised of water (100 mL), ethanol (50 mL), ortho-phosphoric acid (50 mL), isopropyl alcohol (10 mL), and urea (1 g) using a two-electrode system at constant potential of 4.8 V for 60 s. After electropolishing, the copper foil was rinsed with DI water and ethanol, and then dried with a nitrogen flow. Electrodeposition was then carried out in an aqueous solution composed of 5 mM SnSO₄, 20 mM K₄P₂O₇, 1 mM AgNO₃, and 0.1 wt% polyethylene glycol to galvanostatically deposit the AgSn alloy layer on the polished copper substrate at 50 mA for 2 h. All of the chemicals used in electrodeposition were purchased from Sigma-Aldrich. Anodization was performed at 9 V for 60 min in an aqueous solution of 0.05 M oxalic acid (99.5%, J. T. Baker) to synthesize the Ag-doped SnO₂ nanoporous layer (AgSn-NPL). Experiments were carried out at room temperature in a two-electrode set-up with platinum gauze as a counter electrode. The samples were then rinsed with DI water and dried under a nitrogen gas flow.

Characterization

A JEOL 6500F scanning electron microscope (SEM) was used to analyze the morphology of the samples. The crystal structure of the electrodeposited AgSn alloy layer was investigated by X-ray diffraction (XRD) analysis which was performed by a Rigaku D/Max Ultima II (Rigaku Corporation, Japan) configured with a CuK α radiation, graphite monochromator, and scintillation counter. A JEOL 2010 high resolution transmission electron microscope (HRTEM) was used to observe the morphologies and elemental mapping of the samples. Chemical

compositions of the samples were checked by XPS (PHI Quantera XPS, Physical Electronics, USA). An Al anode at 25 W was used as an X-ray source with a pass energy of 26.00 eV, 45° take off angle, and a 100 μm beam size. A pass energy of 140 eV was used for survey and 26 eV for atomic concentration.

Electrochemical measurements

1. Cyclic voltammetry (CV) measurement. The nanoporous layer was directly used as the working electrode without adding any binder or supporting additives. The electrocatalytic ORR and OER tests were performed in O₂-saturated 0.1 M aq NaOH with platinum foil and Hg/HgO (in 0.1 M NaOH, CH Instruments) electrode as counter and reference electrodes, respectively, within a three-electrode set-up. O₂ flow was maintained in the electrolyte throughout the electrochemical measurements. CV was performed at a scan rate of 5 mV s⁻¹. The working electrode was cycled at least 20 times before data were recorded. In a control experiment, CV was also performed in a Ar-saturated 0.1 M aq NaOH through the electrochemical cell. The current density was normalized to the geometric area of the layer and the measured potentials vs Hg/HgO were converted to a reversible hydrogen electrode (RHE) according to the Nernst equation ($E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.0591 \text{ pH} + 0.098$). All the electrochemical characterizations were carried out with an electrochemical analyzer (CHI 608D, CH Instruments, USA).

2. Rotating disk electrode (RDE) measurement. The nanoporous layer was cut into 5 × 5 mm square shapes and then loaded on a glassy carbon rotating disk electrode 5 mm in diameter (Pine Instruments). After loading, Nafion solution (10 wt%) was used to fix the nanoporous layer on the rotating disk electrode. Linear sweep voltammetry (LSV) was measured at 5 mV s⁻¹ with varying rotating speed from 400 rpm to 1600 rpm. Koutecky-Levich plots (J^{-1} vs $\omega^{-1/2}$) were

analyzed at various overpotentials (from 0.4 to 0.55 V). The slopes of their best linear fit lines were used to calculate the electrons transfer number (n) on the basis of the Koutecky-Levich eq 1, 2 and 3:^{S1}

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \quad (1)$$

$$B = 0.62nFC_o(D_o)^{2/3}v^{-1/6} \quad (2)$$

$$J_K = nFkC_o \quad (3)$$

where J is the measured current density, J_K and J_L are the kinetic and diffusion limiting current density, ω is the electrode rotation velocity, n is overall number of transferred electron, F is the Faraday constant, C_o is the bulk concentration of O_2 dissolved in the electrolyte, v is the kinematic viscosity of the electrolyte, and k is the electron transfer rate constant.

3. Electrochemical active surface area (EASA) measurement. The EASA is estimated from the non-Faradaic capacitive current associated with double-layer capacitance (C_{DL}) of the thin-film catalysts from CV curves. The EASA is then calculated by the double-layer capacitance according to eq 4:^{S2}

$$EASA = \frac{C_{DL}}{C_s} \quad (4)$$

where C_s is the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions. An average value of $C_s = 0.060 \text{ mF cm}^{-2}$ is used in this work. The roughness factor (RF) is then calculated by dividing the estimated EASA by the geometric area of the electrode.

Supporting Figures

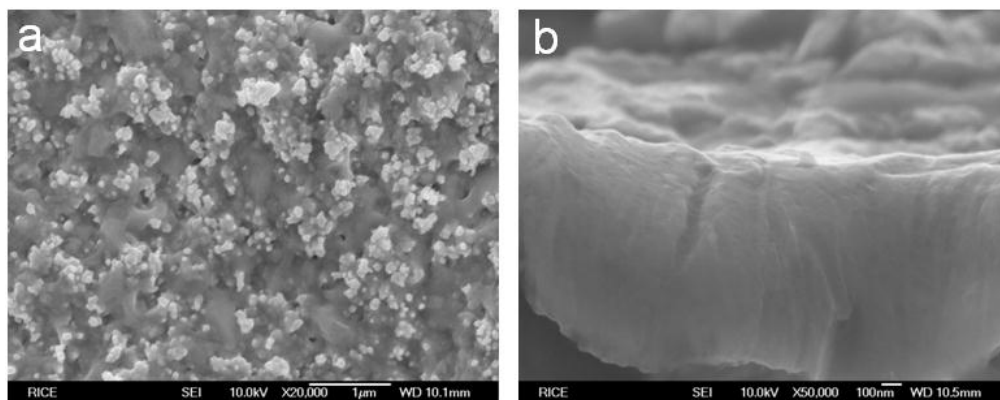


Figure S1. SEM images of the electrodeposited Ag-Sn alloy layer. (a) Top view. (b) Cross-sectional view.

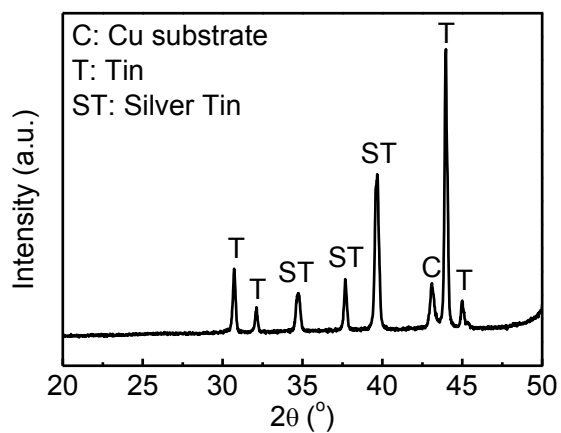


Figure S2. XRD of the electrodeposited Ag-Sn alloy layer. Cu substrate (PDF card # 00-004-0836), Sn (# 00-004-0673) and AgSn (# 00-056-1240) were detected.

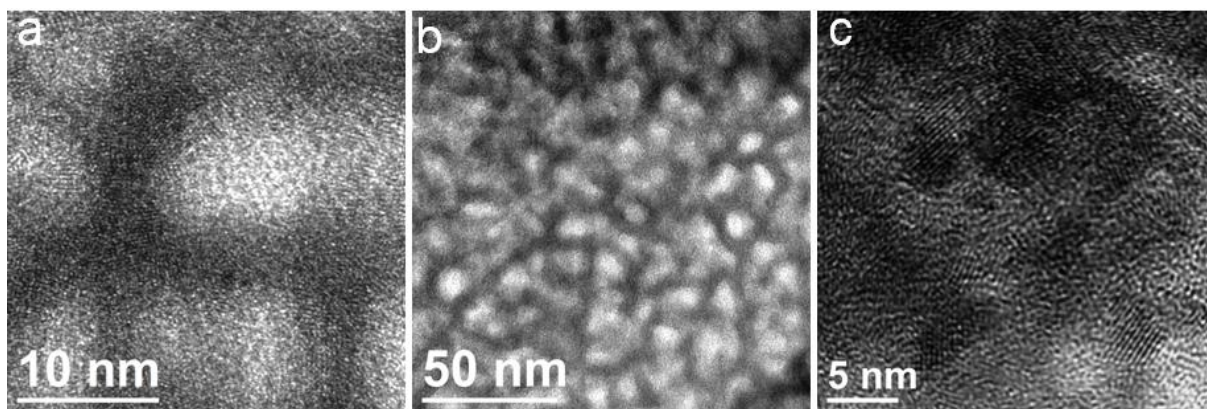


Figure S3. TEM images of the AgSn NPL. (a-c) TEM images with different magnifications.

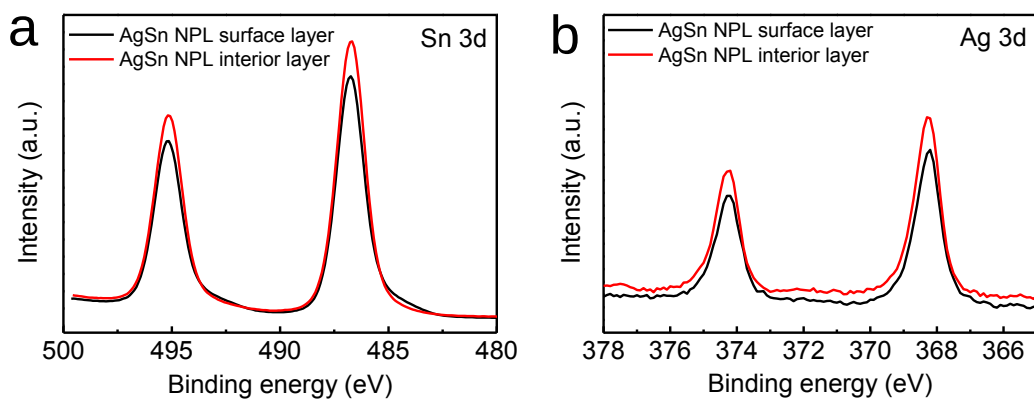


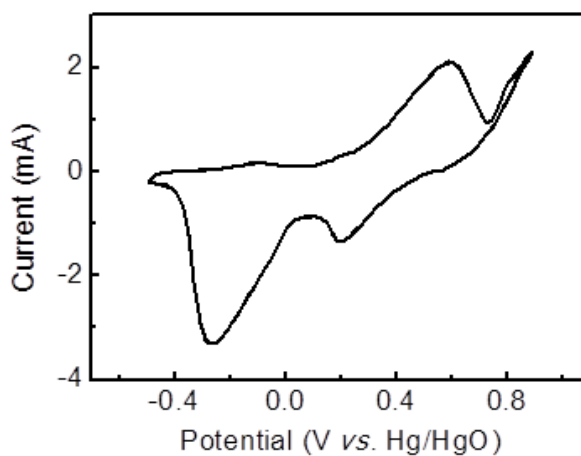
Figure S4. XPS analysis on the surface and interior of the AgSn NPL. (a) Spectra of Sn and (b) spectra of Ag in the surface and interior of the NPL.

Table S1. Ag and Sn content in different samples by XPS analysis

Sample names	Ag content (at%)	Sn content (at%)
AgSn substrate	1.7	98.3
Surface layer of the AgSn NPL	1.7	98.3
Interior layer of the AgSn NPL	1.7	98.3

Table S2. Ag and Sn content in the NPL by XPS analysis deposited from different plating solution concentrations

AgNO ₃ concentration in the plating solution	Ag content (at%)	Sn content (at%)
1 mM	1.7	98.3
0.05 mM	0.3	99.7

**Figure S5. CV voltammogram of the 0.3 at% Ag in AgSn NPL.**

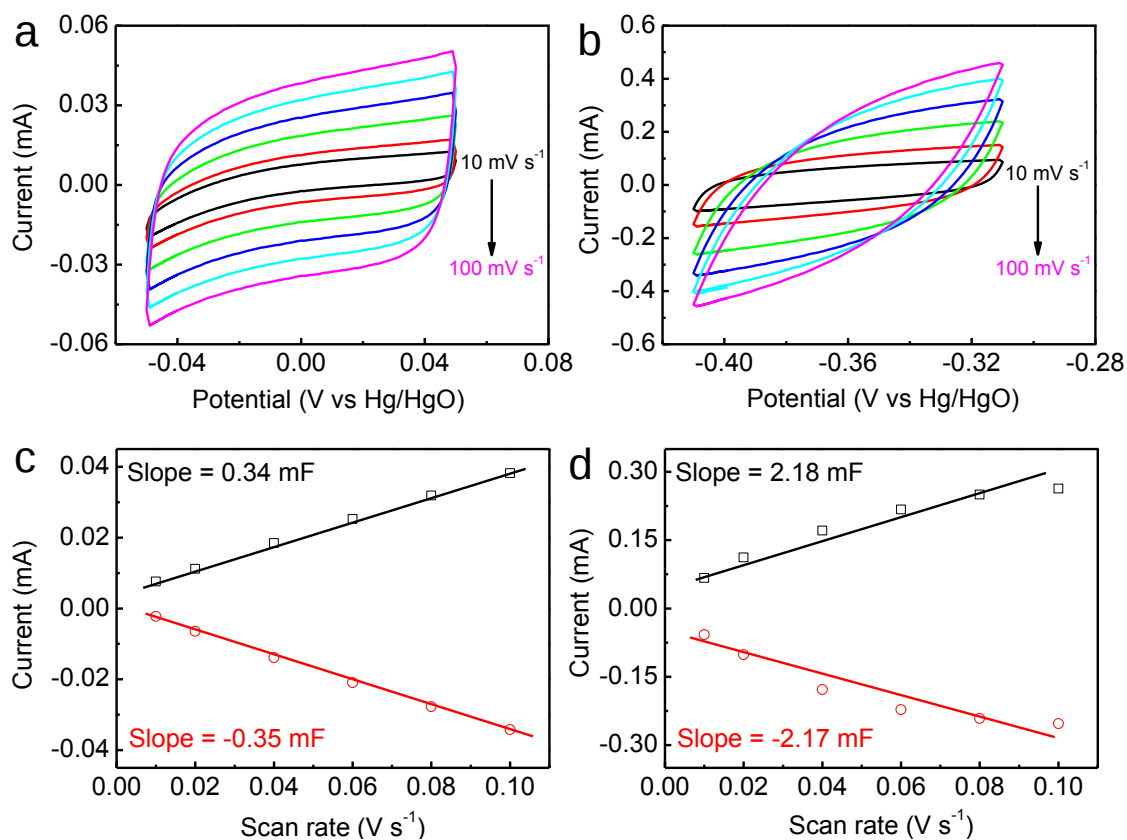


Figure S6. Electrochemical active surface area of the films. (a-b) CV curves of the compact AgSn and AgSn NPL, respectively. (c-d) Capacitance calculation of the compact AgSn and AgSn NPL, respectively.

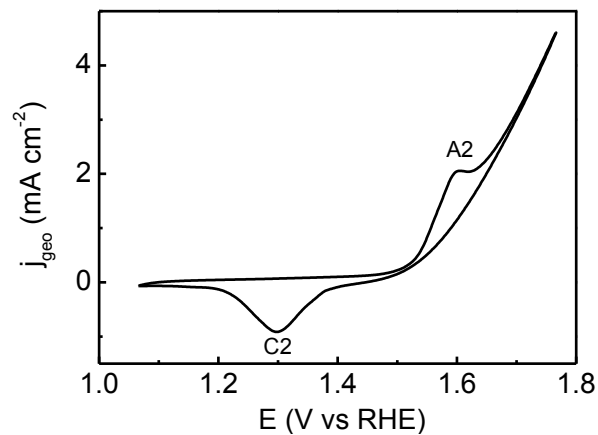


Figure S7. CV voltamogram of the AgSn NPL measured at scan rate of 5 mV s^{-1} to show the OER performance.

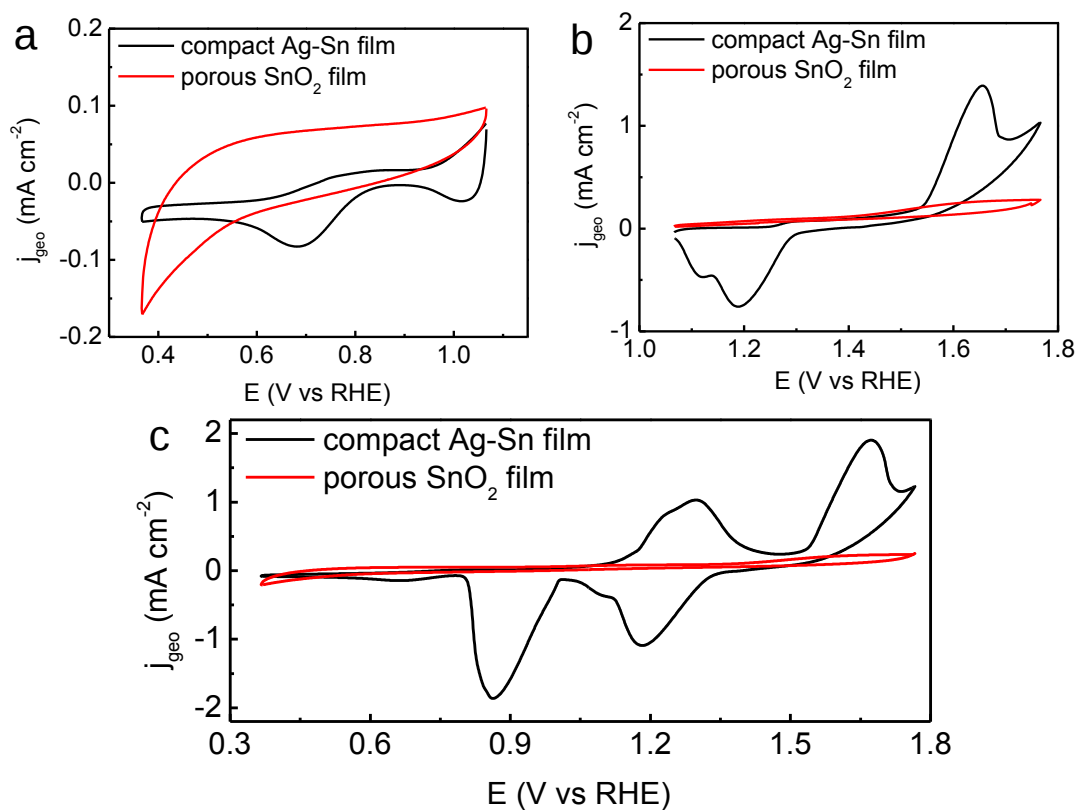


Figure S8. Electrocatalytic performance of the porous SnO_2 thin film and compact Ag-Sn layer: (a) ORR, (b) OER, (c) bifunctional property.

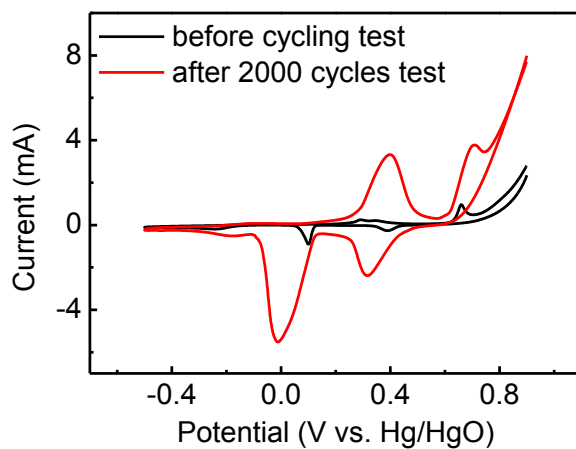


Figure S9. CV curves of the AgSn NPL before (black line) and after (red line) 2000 cycles stability test.

Table S3. Electrocatalytic activities of the AgSn-NPL and the other state-of-the-art oxygen electrodes.

Electrodes	Ag loading ($\mu\text{g cm}^{-2}$)	ORR onset potential (V vs RHE)	<i>n</i> for ORR	Reference
<i>AgSn NPL</i>	<i>3.8</i>	<i>0.87</i>	<i>3.1</i>	<i>This work</i>
Ag nanoclusters	142	0.87	2.3	S3
Ag microparticles	17.1	0.81	3.2	S4
Carbon-supported Ag nanoparticles	20	0.74	1.93	S5
Ag-Co particles	163	---	2.9	S6
Ag/Co ₃ O ₄	64730	---	---	S7
Silver-molybdate	410	---	3.3	S8
FeAgMo ₂ O ₈	---	---	---	S9

References

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