

## Supporting Information

Atomic Sn sites on biomass-derived N-doped porous carbon for  
accelerating oxygen reduction reaction

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## Experimental Section

### General Remarks

All the reagents and solvents were reagent grade and used as received. Powder X-ray diffraction (PXRD) data was collected on a PANalytical Empyrean series 3 diffractometer using Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at room temperature. Transmission electron microscopy (TEM) was measured by JEOL JEM2200FS electron microscope at 100 KV. The high-angle annular dark-field scanning TEM (HAADF-STEM) and elemental mapping images were taken on a JEOL JEM2200FS electron microscope operated at 200 kV. X-ray photoelectron spectra (XPS) data were collected from Thermo Scientific K-Alpha (USA). N<sub>2</sub> adsorption-desorption isotherms were measured on a QuadraSorb SI apparatus at 77 K and the surface areas were calculated by the Brunauer-Emmett-Teller (BET) method. The Raman spectrum was recorded on Edinburgh RM5 spectrometer with a model 100 Ramascope fiber optic instrument. Electrochemical measurements were conducted on the CHI 760E workstation (CH Instruments, Inc.) with a RRDE-3A rotator by employing a typical three-electrode system (the corresponding methods were specified below). The XAFS spectra of the Sn K edge were measured at Japan SPring-8 (Super Photon ring-8 working at 2.5 GeV, with a maximum current of 250 mA). ATHENA in the IFEFFIT software package is used to perform background subtraction, normalization and Fourier transformation on the original EXAFS data. In addition, use the ARTEMIS program to perform least square curve parameter fitting.

**Preparation of Sn-NC.** In a typical synthesis, 0.1 g SnCl<sub>2</sub> and 0.1 g laver were mixed in a mortar and ground evenly for 30 min, and then 0.4 g ZnCl<sub>2</sub> was added into above mortar with continuous grinding for another 30 min. Then, the mixture was added into quartz mortar and heated at 900 °C under a flowing N<sub>2</sub> atmosphere for 2 h. After cooling down, the black powder obtained was added into 0.5 M H<sub>2</sub>SO<sub>4</sub> (100 ml) and stirred for 8 h at 80 °C. A black powder was then separated by filtration, washed with water for three times, and finally dried in vacuum at 60 °C for 3 h, generating Sn-NC.

**Preparation of NC.** Following the above-described preparation of Sn-NC without SnCl<sub>2</sub>, NC was prepared.

**Electrochemical measurement.** LSV and RRDE measurements were conducted on the CHI 760E workstation (CH Instruments, Inc.) with a RRDE-3A rotator (ALS Co., Ltd) in a quartz beaker. A typical three-electrode system was employed to evaluate the electrochemical properties of the prepared catalysts with using a commercial glassy carbon (GC) electrode (4 mm diameter, 0.1256 cm<sup>2</sup>), a carbon rod, and Ag/AgCl electrode (in saturated KCl solution) as the working, counter, and reference electrodes, respectively. All potentials were referred to the reversible hydrogen electrode by adding a value of (0.197 + 0.059×pH) V. All the electrochemical tests in this study were conducted at least three times to ensure the accuracy of the measurement. Besides, the iR correction was applied to get rid of the influence of the Ohmic resistance (the corresponding methods were specified below).

**Preparation of the working electrode.** The catalyst-modified working electrode was fabricated by casting an appropriate amount of catalyst ink, which was obtained by ultrasonically dispersing the catalyst (4 mg) into 1.5 mL ethanol and 0.5 mL deionized water solvent containing 0.5  $\mu\text{L}$  5 wt% Nafion. Then, 8  $\mu\text{L}$  of the mixture was dropped onto a polished glassy carbon electrode (4 mm in diameter). The loaded electrode was placed in a 60  $^{\circ}\text{C}$  oven for 10 min to dry and then was taken out to cool down before all the tests. The loading amount of each catalyst was kept at 80  $\mu\text{g cm}^{-2}$ .

**LSV measurement.** Prior to the test, the electrolyte (0.1 M KOH solution or 0.1 M  $\text{HClO}_4$ ) was bubbled with  $\text{O}_2$  for at least 30 min to make it saturated with  $\text{O}_2$ , and a constant oxygen flow was kept during the measurement. For the LSV measurement, the rotating speed of the working electrode was increased from 400 to 2500 rpm at the scan rate of 10  $\text{mV s}^{-1}$ .

**Rotating ring-disk electrode (RRDE) measurement.** The rotating speed of the working electrode was fixed at 1600 rpm with the scan rate of 10  $\text{mV s}^{-1}$  for the RRDE test. The electron transfer number ( $n$ ) is calculated *via* the following equation.

$$n = 4I_d / (I_d + I_r / N) \quad (1)$$

$$\% \text{HO}^{2-} = 200(I_r / N) / (I_d + I_r / N) \quad (2)$$

Where  $I_d$  stands for the disk current,  $I_r$  represents the ring current, and  $N$  is the current collection efficiency of the Pt ring, which was identified to be 0.43 in 2  $\text{mmol L}^{-1}$   $\text{K}_3\text{Fe}[\text{CN}]_6$  and 0.1 M KCl solution.

**Koutecky-Levich (K-L) plots.** The working electrode was scanned cathodically at the rate of 10 mV s<sup>-1</sup> with the rotation speed from 400 to 2500 rpm. K-L plots ( $J^{-1}$  vs  $\dot{\omega}^{-1/2}$ ) were analyzed according to the K-L equation:

$$1/J = 1/J_L + 1/J_K = 1/(B\omega^{1/2}) + 1/J_K \quad (3)$$

$$B = 0.2nFC_0D_0^{2/3}\nu^{-1/6}; J_K = nFkC_0$$

Where  $J$  is the measured current density,  $J_k$  and  $J_L$  are the kinetic and limiting current densities,  $\dot{\omega}$  is the angular velocity,  $n$  is the transferred electron number,  $F$  (96485 C mol<sup>-1</sup>) is the Faraday constant,  $D_0$  is the diffusion coefficient of O<sub>2</sub> ( $1.9 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>),  $C_0$  is the bulk concentration of O<sub>2</sub> ( $1.2 \times 10^{-6}$  mol cm<sup>-3</sup>),  $\nu$  is the kinetic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>), and  $k$  is the electron-transfer rate constant. The constant 0.2 is adopted when the rotation speed is expressed in rpm.

**iR-Correction.** The iR correction has been adopted to remove the influence of Ohmic resistance on the ORR measurements. Specifically, the electrochemical alternating current impedance spectroscopy (EIS) was utilized to measure the Ohmic resistance under the ORR conditions. The potentials were calculated *via* the following equation:

$$E_{iR\text{-corrected}} = E - iR \quad (4)$$

Where  $i$  is the current,  $R$  is the uncompensated ohmic electrolyte resistance measured *via* high frequency A.C. impedance in O<sub>2</sub>-saturated electrolyte, which is around 10  $\Omega$  and 50  $\Omega$  for 0.1 HClO<sub>4</sub> and 0.1 M KOH solution, respectively.

**Zn-air Battery Tests.** The Zn-air battery measurements were performed with a homemade Zn-air cell. The air cathode includes the hydrophobic carbon paper with a

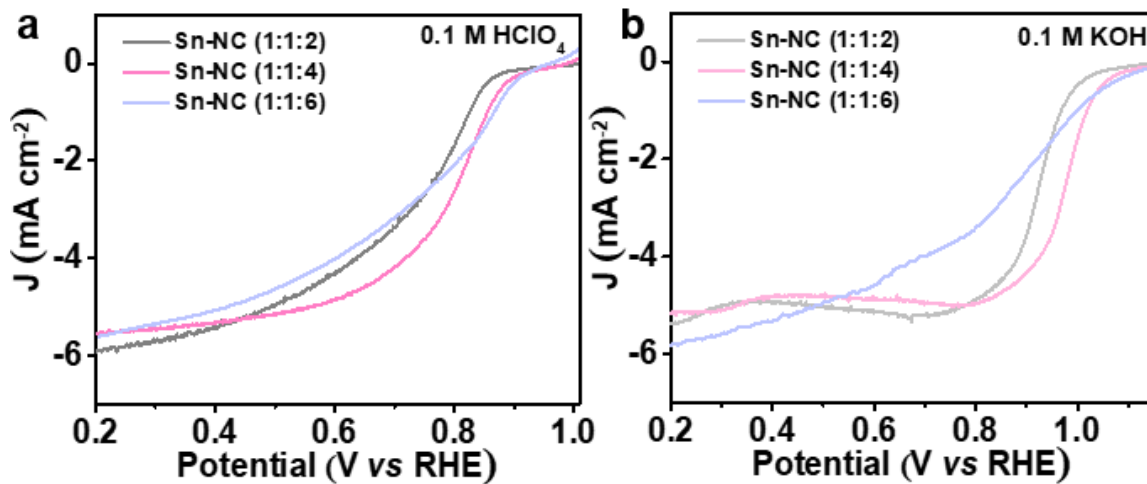
catalyst layer on the electrolyte-facing side and a gas-diffusion layer on the air-facing side. The catalyst ink was dropped and painted onto the carbon paper ( $1.0 \text{ cm}^2$ ) to fabricate the catalyst layer with a catalyst loading of  $5 \text{ mg cm}^{-2}$ . The gas diffusion layer endows the  $\text{O}_2$  could effectively permeate from the ambient air to the catalyst sites. A well-polished Zn plate with a thickness of 0.3 mm was used as the anode. The 0.2 M  $\text{Zn}(\text{Ac})_2 + 6 \text{ M KOH}$  mixed solution was used as the electrolyte.

**Membrane electrode assembly (MEA):** 15 mg catalyst was mixed with 2 mL IPA solution, then 200  $\mu\text{L}$  5 wt% Nafion and deionized water mixed solution was added to the above mixture, followed by ultrasonic treatment for 3 h to form catalyst slurry. Then the catalyst slurry was sprayed on the gas diffusion layer to form gas diffusion electrode (GDE). Finally, the GDE was hot-pressed to Nafion 211 films at  $130 \text{ }^\circ\text{C}$  and 3 MPa to form MEA.

**Catalyst loading:** Sample #1,  $0.2 \text{ mg cm}^{-2}$  20 wt% Pt/C in cathode and  $0.1 \text{ mg cm}^{-2}$  20 wt% Pt/C in anode. Sample #2,  $1.0 \text{ mg cm}^{-2}$  Sn-NC catalyst in cathode and  $0.1 \text{ mg cm}^{-2}$  20 wt% Pt/C in anode.

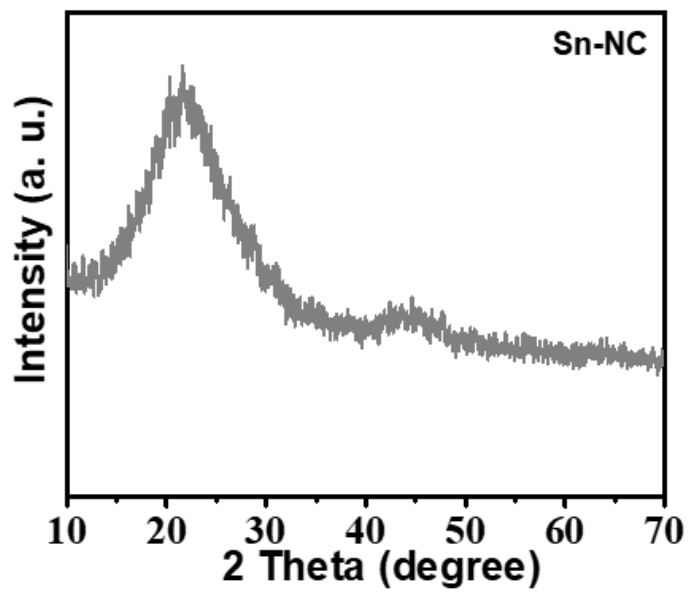
**Fuel cell test:**  $\text{H}_2$  was used as the fuel and  $\text{O}_2$  was used as the oxidant. The MEA was mounted in a single-cell test fixture with a serpentine flow field and a fuel cell clamp (with an active area of  $5 \text{ cm}^2$ ). After the cell activates to a stable value, polarization curves were recorded with the increase in current density regularly. The assembled cell having active area of  $2.5 \times 2.5 \text{ cm}^2$  was operated at  $80 \text{ }^\circ\text{C}$  under relative humidity of 100%

for both anode and cathode.

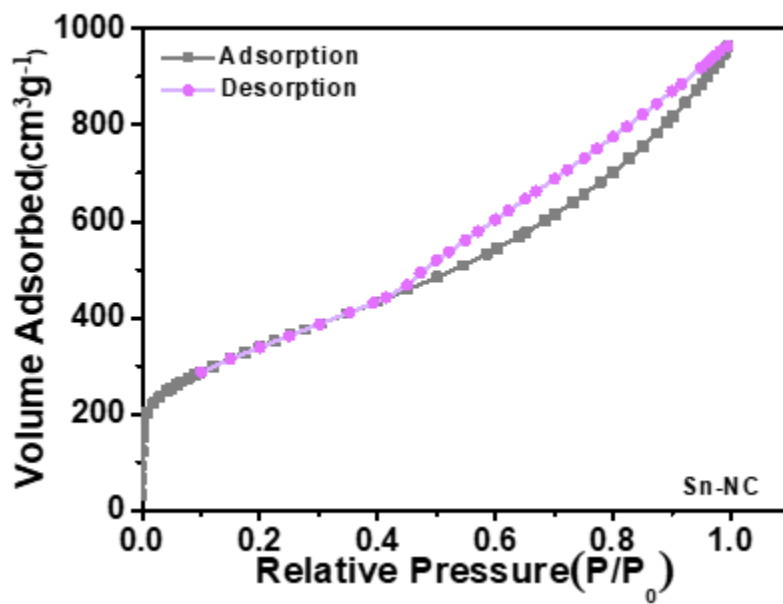


**Figure S1** LSVs for the Sn-NC samples with different mass ratios of SnCl<sub>2</sub>, laver, and ZnCl<sub>2</sub> at 1600 rpm in (a) 0.1 M HClO<sub>4</sub> and (b) 0.1 M KOH.

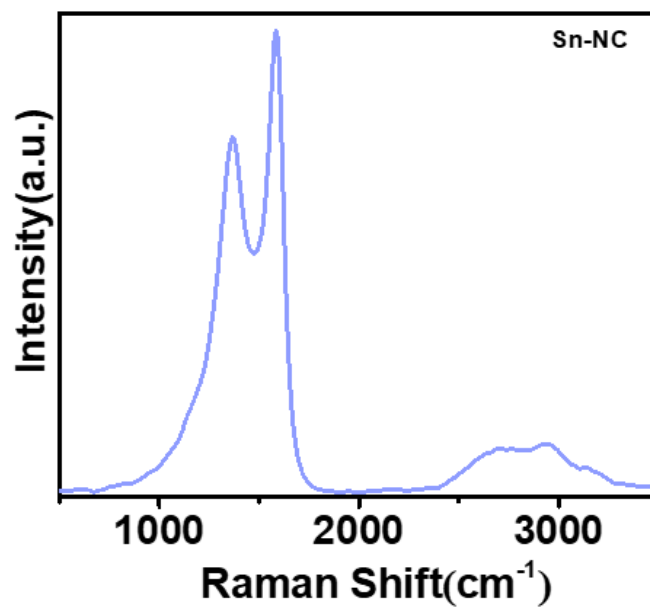




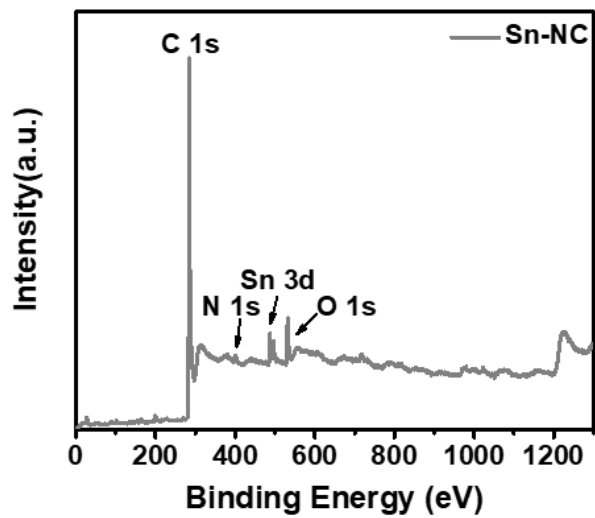
**Figure S2** PXR D of Sn-NC.



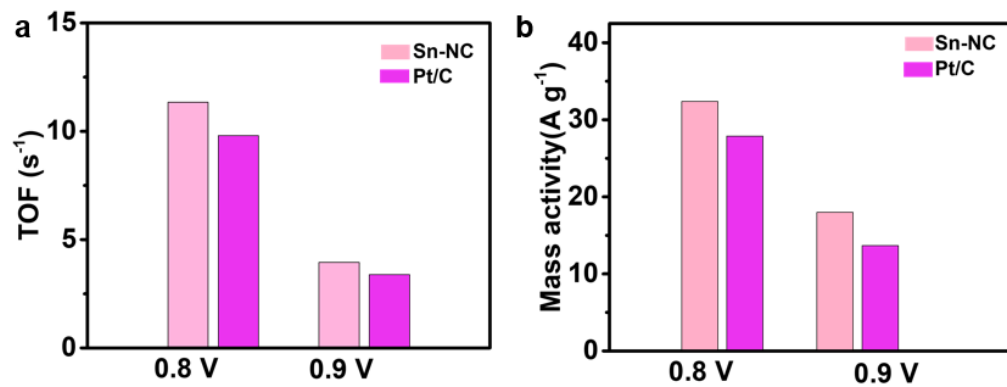
**Figure S3** N<sub>2</sub> adsorption-desorption isotherm of Sn-NC.



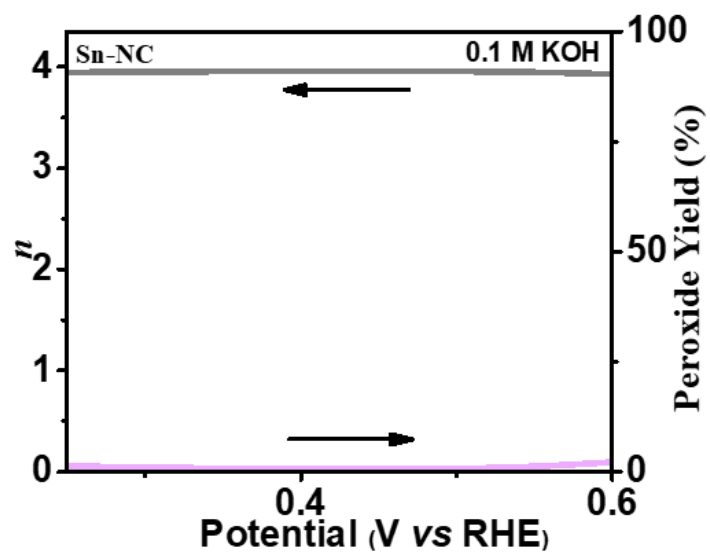
**Figure S4** Raman spectrum of Sn-NC.



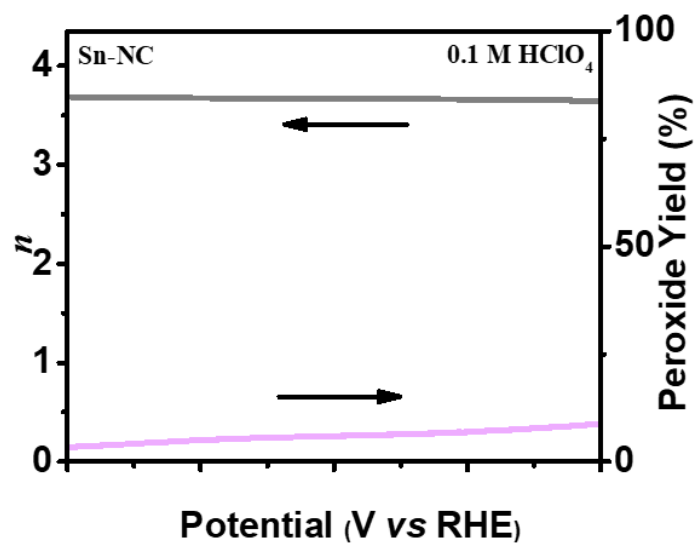
**Figure S5** XPS survey spectrum of Sn-NC.



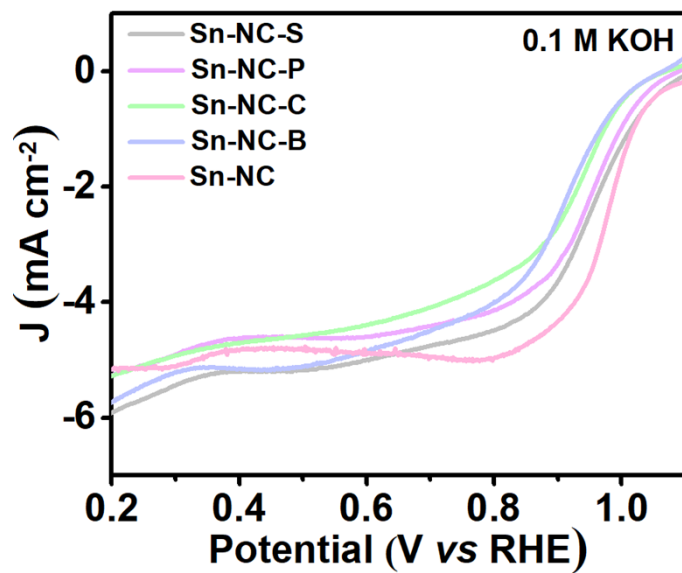
**Figure S6** (a) TOFs and (b) mass activities of Sn NC and PtC at 0.8 and 0.9 V vs RHE in 0.1 M KOH (O<sub>2</sub>-saturated).



**Figure S7**  $\text{H}_2\text{O}_2$  yield curve and  $n$  for Sn-NC in 0.1 M KOH ( $\text{O}_2$ -saturated) under 1600 rpm.

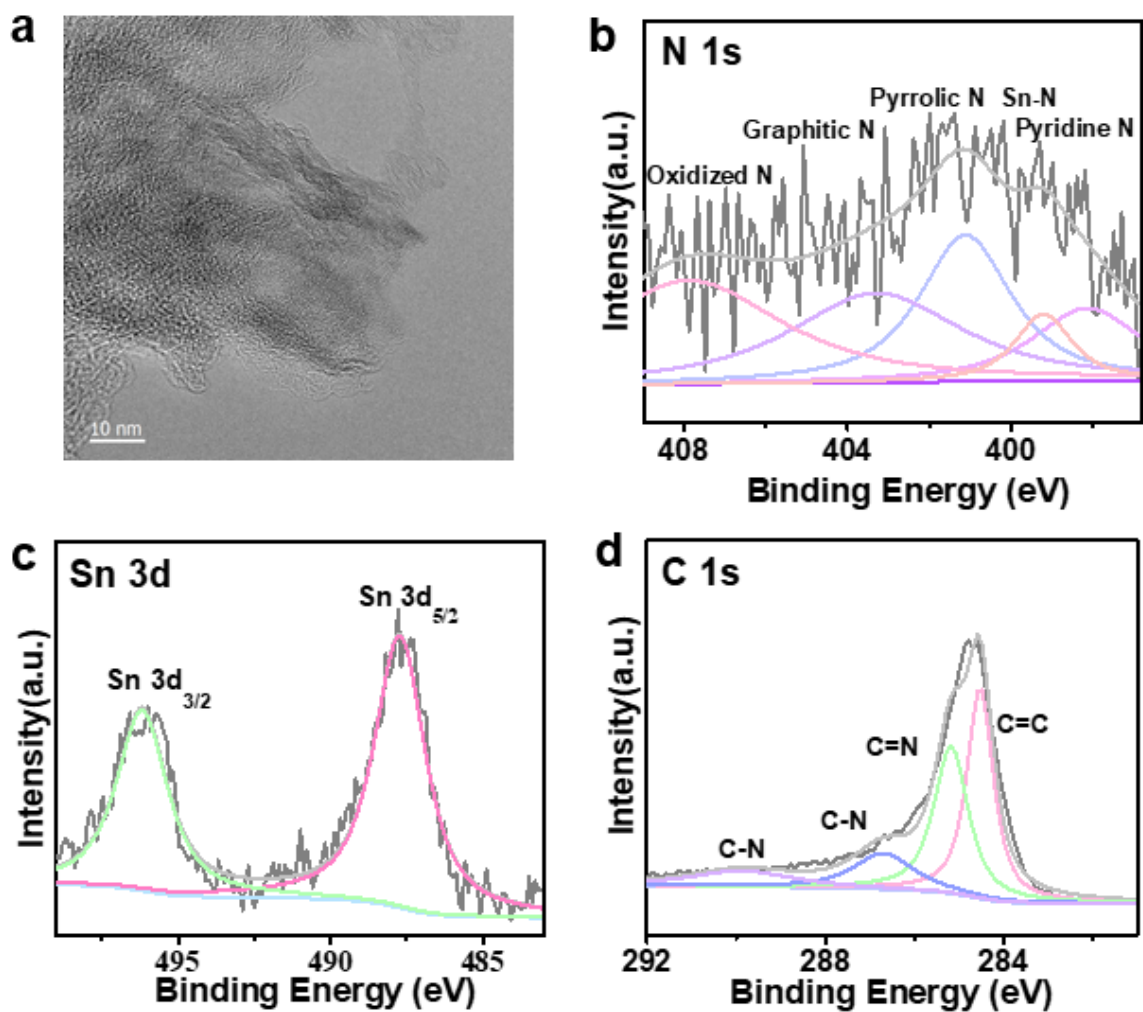


**Figure S8** H<sub>2</sub>O<sub>2</sub> yield curve and n for Sn-NC in 0.1 M HClO<sub>4</sub> (O<sub>2</sub>-saturated) under 1600 rpm.

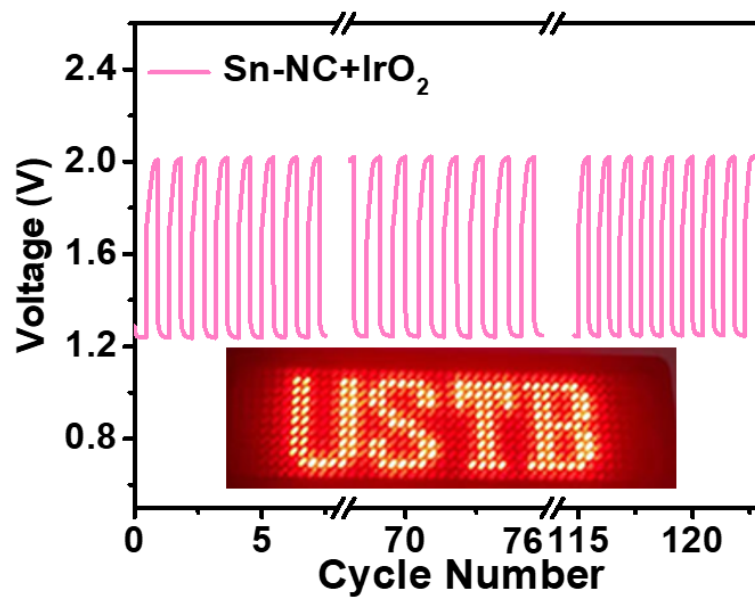


**Figure S9** LSVs for various Sn-N-C catalysts prepared with using laver (named Sn-NC), Sichuan pepper (named Sn-NC-S), Peanut shells (named Sn-NC-P), CNT (named Sn-NC-C), and BP2000 (named Sn-NC-B) as carbon sources in 0.1 M KOH.





**Figure S10** (a) TEM images of Sn-NC after accelerated stress tests in alkaline condition. (b) N 1s, (c) Sn 3d, and (d) C 1s XPS spectra of Sn-NC after accelerated stress tests in alkaline condition.



**Figure S11** Discharge-charge cycling curves of the Sn-NC + IrO<sub>2</sub> Zn-air battery at 5 mA mg<sup>-1</sup>. Inset shows a red LED panel lighted by two Sn-NC + IrO<sub>2</sub> Zn-air batteries.

**Table S1.** Structural parameters obtained from the EXAFS fitting.

<b>Sample</b>	<b>Scattering pair</b>	<b>N</b>	<b>R(Å)</b>	<b><math>\sigma^2</math> (<math>10^{-3}\text{Å}^2</math>)</b>	<b><math>\Delta E_0</math> (eV)</b>	<b>R factor</b>
Sn-N <sub>4</sub>	Sn-N	4	1.53 Å	6.1	1.215	0.01

N is the coordination number; R is interatomic distance (the bond length between central atoms and surrounding coordination atoms);  $\sigma^2$  is Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances);  $\Delta E_0$  is edge-energy shift; R factor is used to value the goodness of the fitting.

**Table. S2.** Comparison of ORR electrocatalytic performance of various nonprecious metal catalysts in 0.1 M KOH and 0.1 M HClO<sub>4</sub>.

<b>Catalyst</b>	<b>Rotation rate</b>	<b>Electrolyte</b>	<b>E<sub>onset</sub> (V vs RHE)</b>	<b>E<sub>1/2</sub> (V vs RHE)</b>	<b>Reference</b>
Sn-NC	1600 rpm	0.1 M KOH	1.08	0.98	this work
Sn <sub>4</sub> XC72	1600 rpm	0.1 M KOH	Not given	0.790	[S1]
SACs-Mn-1000@g-C <sub>3</sub> N <sub>4</sub>	1600 rpm	0.1 M KOH	0.95	0.863	[S2]
Fe-SA/BNC	1600 rpm	0.1 M KOH	1.02	0.910	[S3]
A-CoN <sub>3</sub> S <sub>1</sub> @C	1600 rpm	0.1 M KOH	1.001	0.901	[S4]
Zn-NSC	1600 rpm	0.1 M KOH	1.04	0.9	[S5]
Sn-NC	1600 rpm	0.1 M HClO <sub>4</sub>	0.93	0.82	this work
Sn <sub>4</sub> XC72	1600 rpm	0.1 M HClO <sub>4</sub>	Not given	0.75	[S1]
SACs-Mn-1000@g-C <sub>3</sub> N <sub>4</sub>	1600 rpm	0.1 M HClO <sub>4</sub>	Not given	0.863	[S2]
Fe-SA/BNC	1600 rpm	0.1 M HClO <sub>4</sub>	0.90	0.81	[S3]
A-CoN <sub>3</sub> S <sub>1</sub> @C	1600 rpm	0.1 M HClO <sub>4</sub>	Not given	0.71	[S4]
Zn-NSC	1600 rpm	0.1 M HClO <sub>4</sub>	0.875	0.805	[S5]

## References

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