Supplementary Information

3D Interconnected Nitrogen-self-doped Carbon Aerogels Derived from Biomass Gelatin as Electrocatalysts for Oxygen Reduction Reaction

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1. Experimental section

1.1. Synthesis of 3D interconnected NSCAs electrocatalysts

All reagents used in this experiment are of analytical grade without any further purification. Biomass gelatin and the sodium chloride (NaCl) were purchased from Hebei Taixin chem. Co. and Ningbo Carlo Chemical Reagent Co., respectively. In a typical synthesis process, 2 g of NaCl was dissolved into 50 mL of deionized water by magnetic stirring until it completely dissolved. Thereafter, 1 g of biomass gelatin was dissolved in the above solution and heated to 80 °C until the solution becomes a yellowish and transparent hydrogel. The as-obtained homogeneous hydrogel was then frozen in a refrigerator at -45 °C for 72 h to obtain aerogel. Subsequently, the freeze-dried aerogel was ground to powders and then subjected to pyrolysis. During the pyrolysis process, the aerogel powders were put in a quartz boat located in a tubular furnace under a flow of N_2, and carbonized for 30 min after reaching the desired   temperatures (700, 800, 900 °C), which heating rate is 5 °C min^{-1}. Afterward, the NaCl remained in the carbonized products were removed by deionized water to obtain 3D interconnected nitrogen-self-doped carbon aerogels, named as NSCA-700, NSCA-800, and NSCA-900, respectively.

1.2. Physical characterization

Scanning electron microscopy (SEM) images were taken by a JEOL JSM-7500F field emission scanning electron micro-analyzer, and transmission electron microscopy (TEM) images were taken by a JEOL-2010 electron microscope. The elemental composition was conducted on an energy dispersive spectroscopy (EDS). Raman micro-spectroscopy were obtained with a DXR Raman microscope (LabRAM HR 800) with 532 nm excitation laser. The nitrogen adsorption-desorption isotherms were taken using an ASAP2020 volumetric adsorption analyzer of liquid nitrogen at 77 K. The specific surface area (S_{BET}) and pore size distribution (PSD) of the NSCAs were determined using the Brunauer-Emmett-Teller (BET) method. The element binding environment and surface chemical composition of the NSCAs were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). X-ray diffraction (XRD) patterns were performed using an AXS X-ray diffractometer (Bruker) with a Cu Kα radiation.

1.3. Electrochemical characterization

For the preparation of catalyst ink, 5 mg of the as-prepared NSCA catalyst was dispersed into 20 μL of Nafion solution (5 wt%) and 1 mL ethanol under sonication to obtain uniform suspensions. Next, 12 μL of the above suspensions were added dropwise onto the surface of the working electrode (glassy carbon disk). The commercial Pt-loaded carbon catalyst (Pt/C, 20 wt%) ink was prepared as the reference standard (20 μg cm^{-2}). The electrodes were subsequently dried at room temperature for 20 min.

The electrochemical measurements were conducted using a computer-controlled electrochemical test instrument (CHI 750E, Shanghai.) in O_2-saturated 0.1 M KOH electrolyte with a three-electrode system. A Pt wire was acted as the counter electrode, and an Ag/AgCl (KCl, 3.5 M) electrode was employed as the reference electrode. A rotating disk electrode (RDE) and a rotating ring-disk electrode (RRDE) were performed as the working electrode for cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurements with a computer-controlled potentiostat (Pine Instrument Co.). Before the electrochemical tests, the 0.1 M KOH electrolyte was bubbled by using high-purity Ar or O_2 for 20 min at 25 °C.

In the case of the CV measurement, the potential range was cyclically performed from 0 to 1.1 V (vs. Ag/AgCl) in 0.1 M KOH electrolyte with a sweep rate of 100 mV s^{-1} for 50 cycles for activating

electrode and 10 mV s^{-1} for 2 cycles for recording data. In the case of the LSV measurement, the potential range was conducted from 0 to 1.1 V (vs. Ag/AgCl) in O$_2$-saturated 0.1 M KOH electrolyte with a sweep rate of 10 mV s^{-1} at different rotating speeds of 100, 225, 400, 625, 900, 1225, 1600, 2025 and 2500 rpm. For the RRDE tests, a glassy carbon disk (0.2475 cm^2) was surrounded by a Pt ring (0.1866 cm^2), which was used as a working electrode. The ring current and disk current were collected in O$_2$-saturated 0.1 M KOH solution from RRDE test, respectively. RDE and RRDE tests used Autolab Model.

The measured potentials of the Ag/AgCl reference electrode were converted to the reversible hydrogen electrode (RHE) based on the following equation:

$$V_{RHE} = V_{Ag/AgCl} + V_{Ag/AgClvsNHE} + 0.059\,pH \qquad \text{(Eq. 1)}$$

The number of electrons transferred (n) and %H$_2$O$_2$ released yield during the ORR process by RRDE were calculated as following equations:

$$n = \frac{4\,I_d}{(I_d + I_r)/N} \qquad \text{(Eq. 2)}$$

$$\%H_2O_2 = \frac{200I_r/N}{I_d + I_r/N} \qquad \text{s(Eq. 3)}$$

where I_d is the disk electrode current, and I_r is the ring electrode current, respectively. N (the value is 0.38) is the collection efficiency of the Pt ring.

To calculate the n for the ORR process by RDE measurement, we applied the following Koutecky-Lecich (K-L) equations:

$$j^{-1} = j_K^{-1} + j_L^{-1} \qquad \text{(Eq. 4)}$$

$$j^{-1} = j_k^{-1} + B^{-1}\omega^{-1/2} \qquad \text{s(Eq. 5)}$$

$$B = 0.62nFC_0(D_0)^{2/3}v^{-1/6} \qquad \text{(Eq. 6)}$$

where j_L is the limiting current density of reactive species reaction by the diffusion controlled process, and j_K is the kinetic-limiting current density, respectively. F is the Faraday constant (96486.4 C mol^{-1}), C$_O$ is the concentration of O$_2$ in 0.1M KOH electrolyte (1.21 × 10^{-3} mol L^{-3}), D$_O$ is the coefficient of O$_2$ in 0.1 M KOH electrolyte (1.9 ×10^{-5} cm^2 s^{-1}), ω (rad s^{-1}) is the rotation rate of the electrode, A (cm^2) is the electrode area, and v is the kinematic viscosity of the 0.1 M KOH electrolyte (0.01 cm^2 s^{-1}).
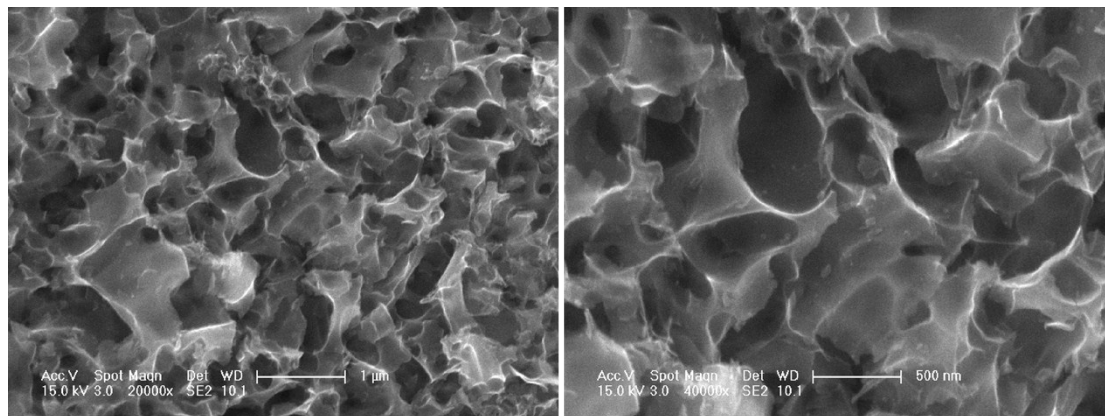
2. Table and Figures

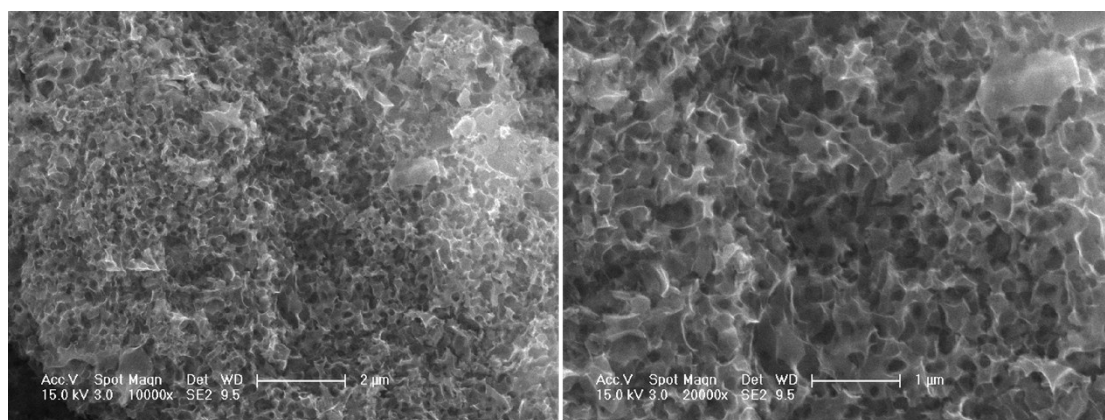**Figure S1:** SEM images of the NSCA-700 sample.

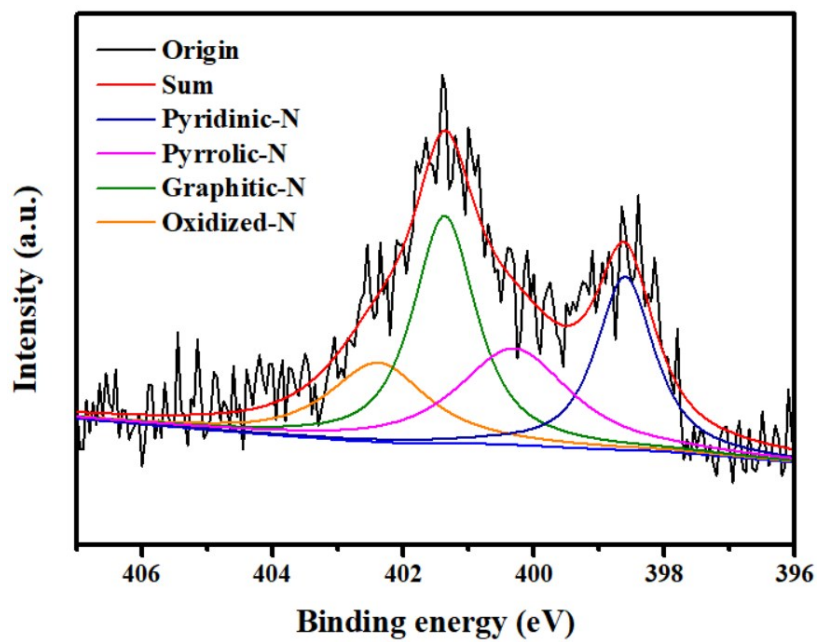**Figure S2:** SEM images of the NSCA-900 sample.

Figure S3: The high-resolution N 1s spectra of the NSCA-700 sample.
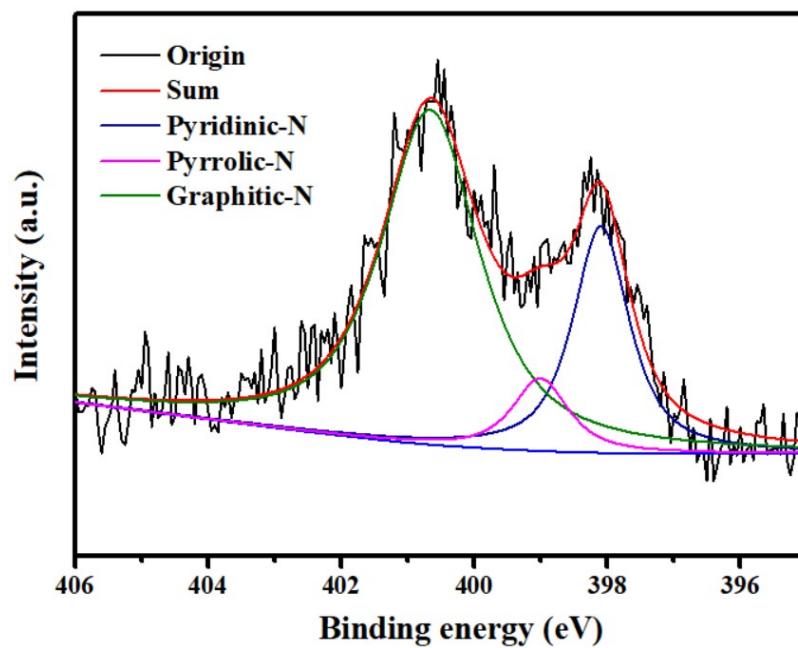

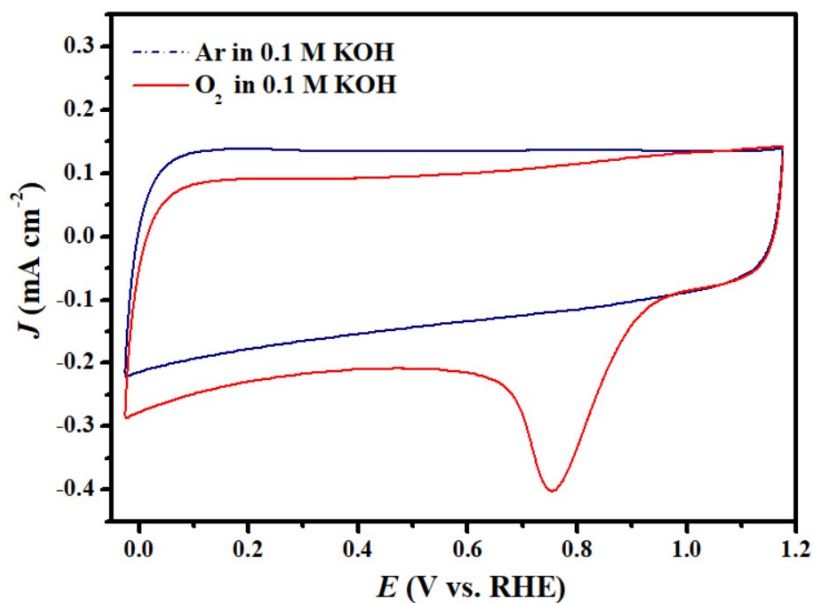**Figure S4:** The high-resolution N 1s spectra of the NSCA-900 sample.

Figure S5: Cyclic voltammetry (CV) curves of the NSCA-800 catalyst in Ar-saturated and O_2-saturated 0.1 M KOH electrolyte.
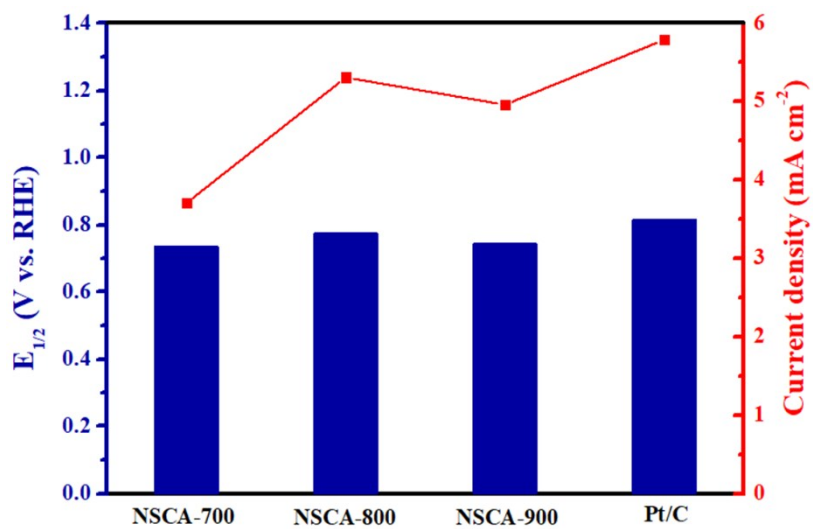

Figure S6: Dependence of half-wave potential ($E_{1/2}$) and limiting current densities on the NSCA-700, NSCA-800, NSCA-900, and commercial Pt/C catalysts.

Table S1. Summary of calculated results from nitrogen adsorption-desorption analysis and chemical composition analysis from XPS measurements.

Sample	S_{BET} (m^2 g^{-1})	Pore volumes (cm^3 g^{-1})	at.% (C)	at.% (N)	at.% (O)

NSCA-700	376	0.34	89.11	5.73	5.16
NSCA-800	839	0.67	89.09	5.03	5.88
NSCA-900	795	0.64	89.64	4.69	5.67