Supporting Information

Carbon nanosheet-supported CrN nanoparticles as efficient and robust oxygen reduction electrocatalysts in acidic media and seawater Zn-air batteries

Yating Zhang[a], Haoming Wu[a], Jun Ma[c], Junming Luo[a, *], Zhe Lu[a], Suyang Feng[a], Yijie Deng[b, *], Hui Chen[a], Qi Wang[a], Zhengpei Miao[a], Peng Rao[a], Neng Yu[d], Yuliang Yuan[a], Jing Li[a], and Xinlong Tian[a, *]

[a]*School of Marine Science and Engineering, Hainan Provincial Key Lab of Fine Chemistry, Hainan University, Haikou 570228, China*

[b]*School of Resource Environment and Safety Engineering, University of South China, Hengyang 421001, China*

[c]*School of Materials Engineering, Jiangxi College of Applied Technology, Ganzhou 341000, China*

[d]*State Key Laboratory of Nuclear Resources and Environment, East China University of Technology, Nanchang 330013, China*

*****Corresponding authors: Jumming Luo (luojunming@hainanu.edu.cn), Yijie Deng (dengyijie19891009@163.com), and Xinlong Tian (tianxl@hainanu.edu.cn)

1 Experimental section

1.1 Synthesis of catalysts

Synthesis of Cr_2O_3/C. Cr_2O_3/C materials were prepared by dispersing 1.68 g of dicyandiamine (DCDA) and 0.077 g of chromium (III) acetylacetonate ($Cr(acac)_3$) into a quantitative amount of anhydrous ethanol, stirring for 4 h at room temperature to form a homogeneous solution, and then the solution was dried in an oil bath at 75 °C for 10 h to obtain a purple pink precursor. The precursor was annealed at 650°C for 2 h in a N_2 gas to obtain the Cr_2O_3/C materials.

Synthesis of CrN/CNS. CrN/CNS materials were prepared by dispersing 1.68 g of DCDA and 0.077 g of $Cr(acac)_3$ into a quantitative amount of anhydrous ethanol, stirring for 4 h at room temperature to form a homogeneous solution, and then the solution was dried in an oil bath at 75 °C for 10 h to obtain a purple pink precursor. The precursor was heated in a N_2 gas via a consecutive two-step pyrolysis procedure: first annealed at 650°C for 2 h, and then annealed at 750-850°C for 2 h to obtain the CrN/CNS-T catalysts (T represents the annealing temperature at the second step).

Synthesis of CrN/CNS-800#1. CrN/CNS-800#1 materials were prepared by dispersing 1.68 g of DCDA and 0.077 g of $Cr(acac)_3$ into a quantitative amount of anhydrous ethanol, stirring for 4 h at room temperature to form a homogeneous solution, and then the solution was dried in an oil bath at 75 °C for 10 h to obtain a purple pink precursor. The precursor was annealed at 800°C for 2 h in a N_2 gas to obtain the CrN/CNS-800#1 catalysts.

1.2 Characterization of Catalysts

X-ray diffraction (XRD) was tested on a DX-2700BH instrument with operating conditions of 40 kV and 40 mA, using a copper target as the X-ray light pipe. Transmission electron microscopy (TEM) images and high-resolution TEM (HR-TEM) images were obtained on a thermoscientific Talos F200X G2 unit. Scanning electron microscopy (SEM) images were performed using a field emission scanning electron microscope (FESEM, Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) was tested on a Thermo

Scientific ESCALAB Xi model. Raman spectroscopy was performed on a high-resolution confocal microlaser Raman instrument, WiTech alpha300R, with a 532 nm laser. Brunauer-Emmett-Teller (BET) surface area and pore structure were tested on an automatic specific surface and porosity analyzer (Micromeritics ASAP 2460, United States). O_2-TPD measurements were performed on an AutoChem1 II 2920. All samples were first dried and pre-treated at 200 °C for 1 h in a He gas stream, then cooled to room temperature, and then fed with a 10% O_2/He mixture (50 mL/min) for 2 h until saturation. After cleaning the unabsorbed O_2 by a He gas, the test sample was heat to 700 °C at a rate of 10 °C/min and the desorption gas was detected by thermal conductivity detector (TCD).

1.3 Electrochemical Measurements

The ORR performance of catalysts was tested in a 0.1 M $HClO_4$ solution at room temperature, using an AUTOLAB M204 workstation and a PINE rotating disk electrode (RDE) system in a three-electrode cell which consists of a glassy carbon (GC)-based working electrode (0.196 cm^2), a graphite rod counter electrode and an Ag/AgCl (saturated-KCl solution) reference electrode. The catalyst-loaded GC electrodes were all prepared in the following procedure: 5 mg of catalyst was mixed with 1 mL of 0.25 wt% Nafion ethanol solution and sonicated for 30 min to form a catalyst ink, then 20 and 25.2 μL of the catalyst ink were dropped onto GC electrodes in the RDE test and the rotating ring disk electrode (RRDE) test, respectively, and finally the catalyst ink on GC electrodes were dried naturally. The catalyst loading in RDE tests was 0.51 mg cm^{-2}.

The RRDE test (0.247 cm^2 GC disk, 0.180 cm^2 Pt ring) was used to investigate the electron transfer mechanism of the ORR. The potential of the Pt ring was kept at 1.1 V vs. RHE. The number of electron transfers (n) was calculated from $n = 4*I_{disk}/(I_{disk}+(I_{ring}/N))$ and the H_2O_2 yield was calculated from H_2O_2 (%) $= (200*I_{ring}/N)/(I_{disk}+(I_{ring}/N))$, where I_{disk} and I_{ring} are the absolute disc and ring currents, respectivily, and N (N = 0.37) is the collection efficiency at the ring electrode.

1.4 Seawater ZABs tests

CrN/CNS-800-based ZABs was fabricated as follows: a polished Zn plate (34.5 mm*85 mm*0.65 mm) and a commercial carbon paper coated with CrN/CNS-800 was employed as anode and air-cathode, respectively, the electrolyte was 0.5 M NaCl solution and natural seawater, respectively. Natural seawater used in the ZABs was adopted from the open sea of Wanning city in Hainan province (18°47'42.51" N, 110°23'27.86" E) without any pretreatment or purification. The CrN/CNS-800-based air-cathode is prepared by coating a certain amount of catalyst ink of CrN/CNS-800 drop by drop on a commercial carbon paper. The catalyst loading of CrN/CNS-800 on the air-cathode of ZABs was 2 mg cm^{-2}. The actual working area of the air cathode was 1 cm^2. The polarization curves and open circuit potential were tested by an electrochemical workstation (AUTOLAB M204). The galvanostatic discharge was conducted on an LANHE (CT2001A) battery testing system.

2 Figures

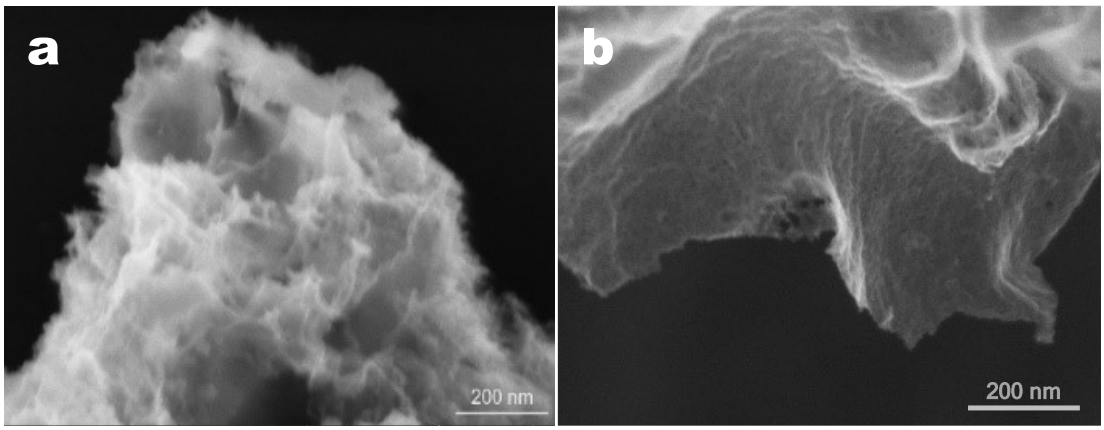

Figure S1. SEM images of (d) Cr_2O_3/C and (e) CrN/CNS-800.

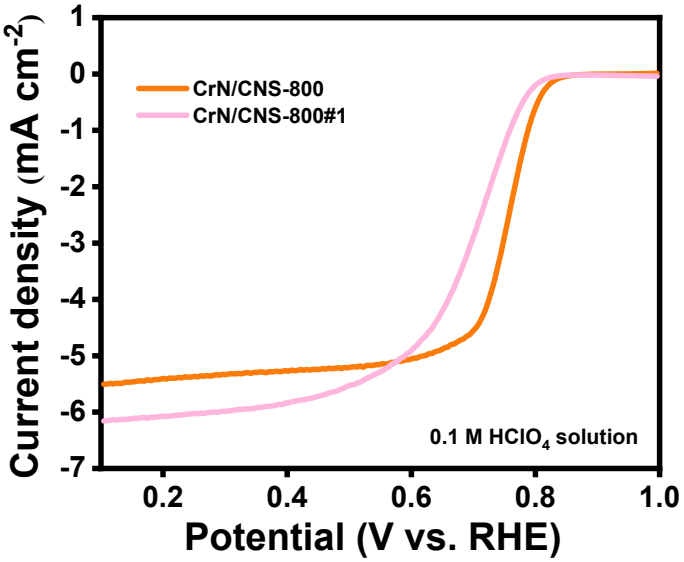

Figure S2. Comparison of ORR activity of CrN/CNS-800 and CrN/CNS-800#1 in 0.1 M $HClO_4$ solution (1600rpm, 10mV·s^{-1}, O_2-N_2).

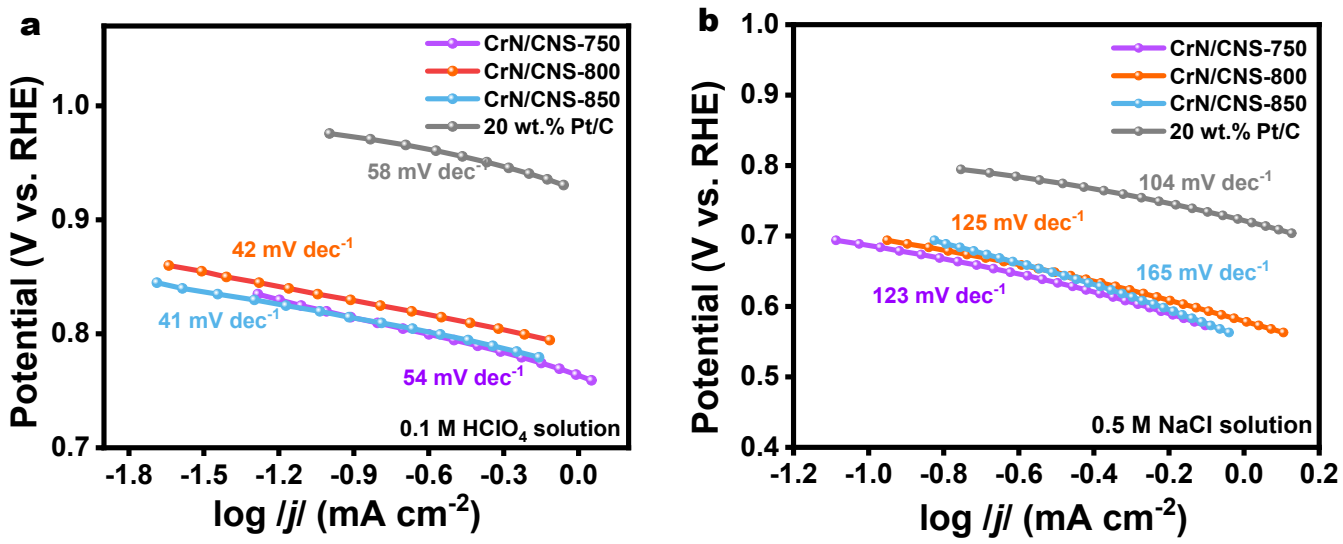

Figure S3. Tafel slopes of CrN/CNS materials and 20 wt.% Pt/C: (a) in acidic media, (b) in the simulated seawater.

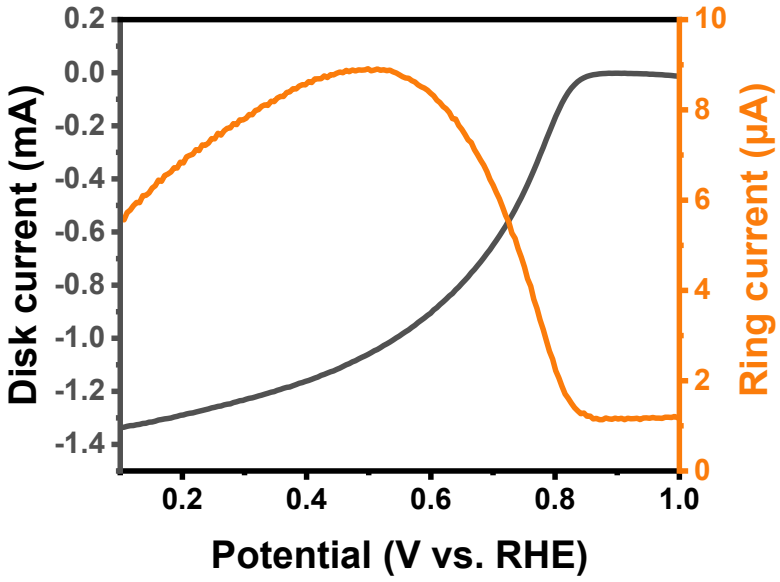

Figure S4. Disk and ring current of CrN/CNS-800 during RRDE tests in 0.1 M $HClO_4$ solution, calculated by subtracting the polarization curve in Ar-saturated solution from the polarization curve in O_2-saturated solution, 10 mV s^{-1}, 1600 rpm.

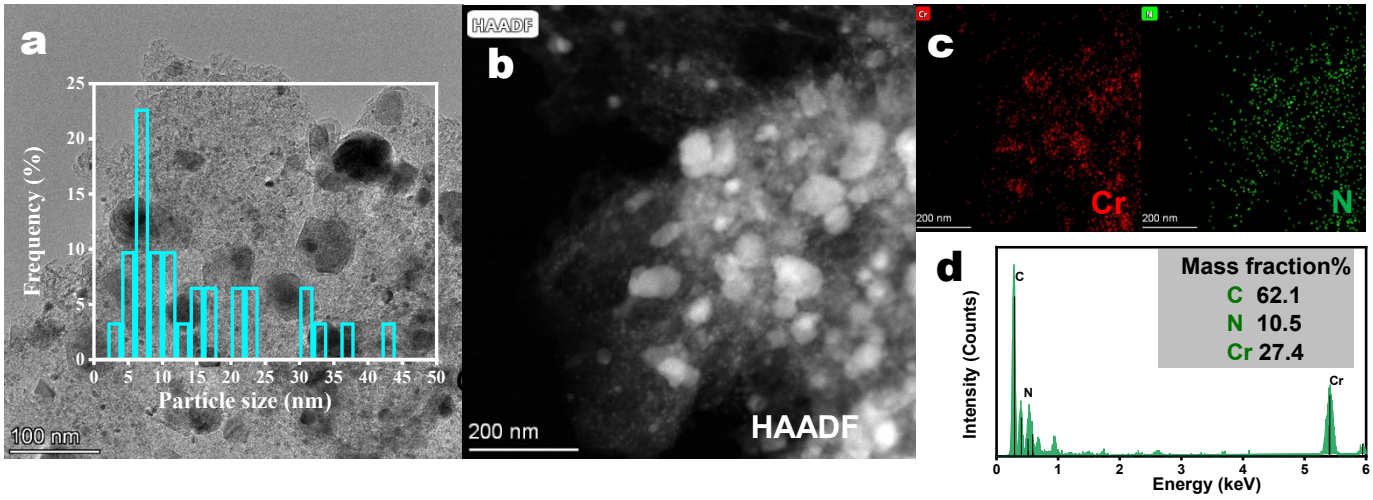

Figure S5. (a) TEM image of CrN/CNS-800 after stability test. (b) HAADF image of CrN/CNS-800 after stability test. (c) EDS Mapping image of CrN/CNS-800 after stability test. (d) EDX profile of CrN/CNS-800 after stability test.

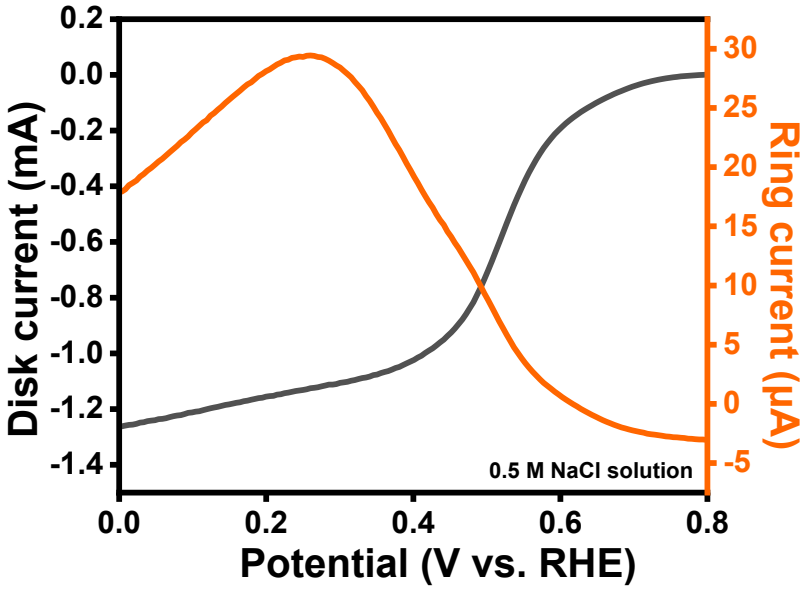

Figure S6. Disk and ring current of CrN/CNS-800 during RRDE tests in 0.5 M NaCl solution, calculated by subtracting the polarization curve in Ar-saturated solution from the polarization curve in O_2-saturated solution, 10 mV s^{-1}, 1600 rpm.

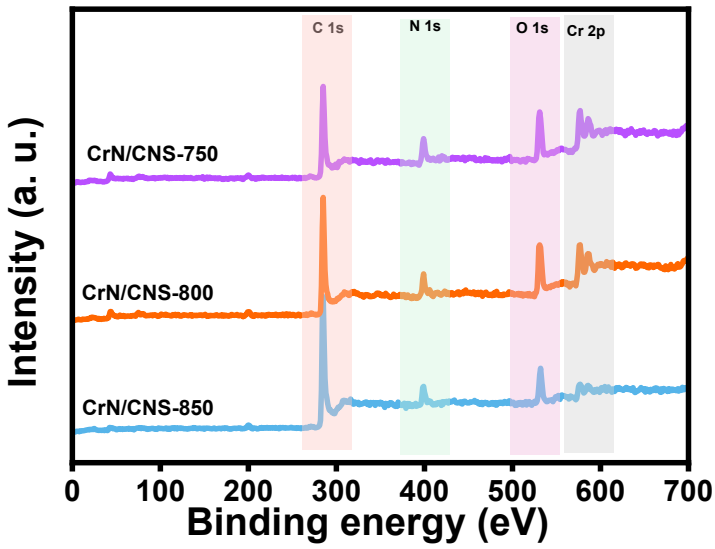

Figure S7. XPS survey spectra of CrN/CNS-750, CrN/CNS-800 and CrN/CNS-850.

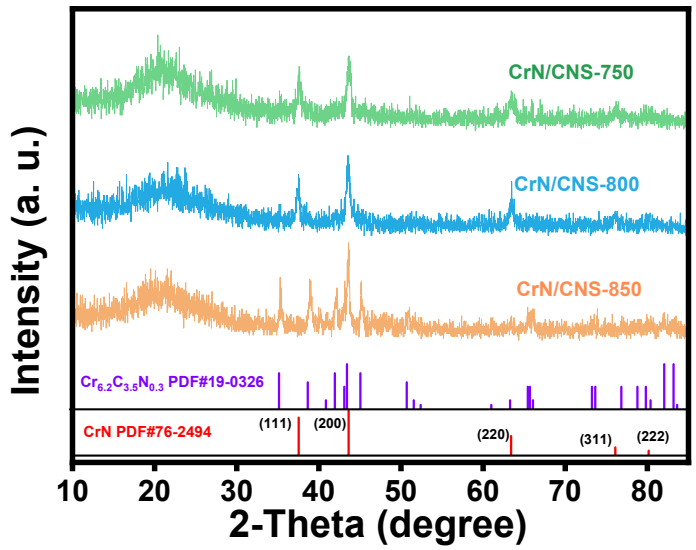

Figure S8. Comparison of XRD patterns of CrN/CNS-750, CrN/CNS-800 and CrN/CNS-850.

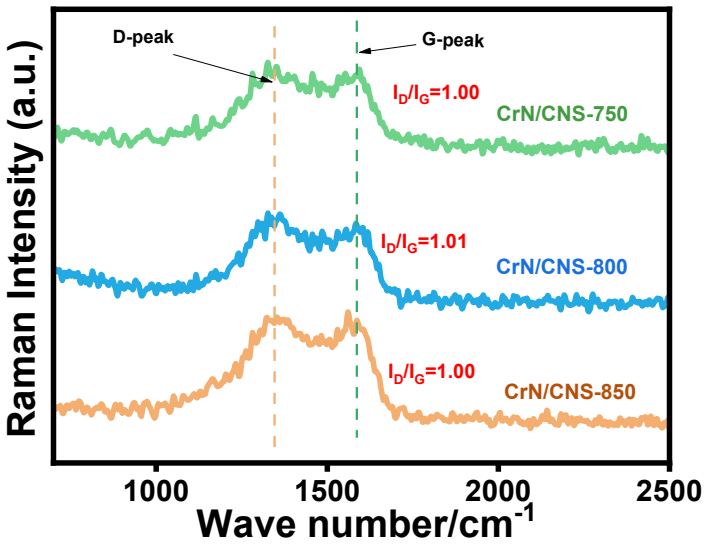

Figure S9. Raman spectra of CrN/CNS-750, CrN/CNS-800 and CrN/CNS-850.

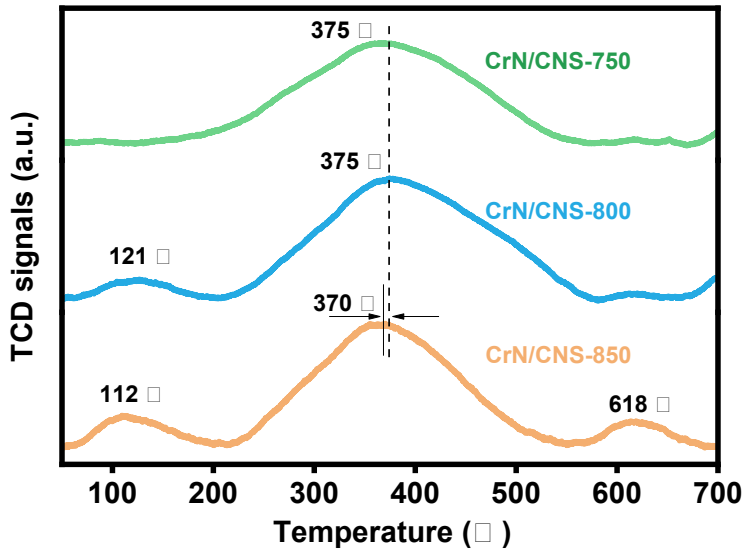

Figure S10. O_2-TPD curves of CrN/CNS-750, CrN/CNS-800 and CrN/CNS-850.

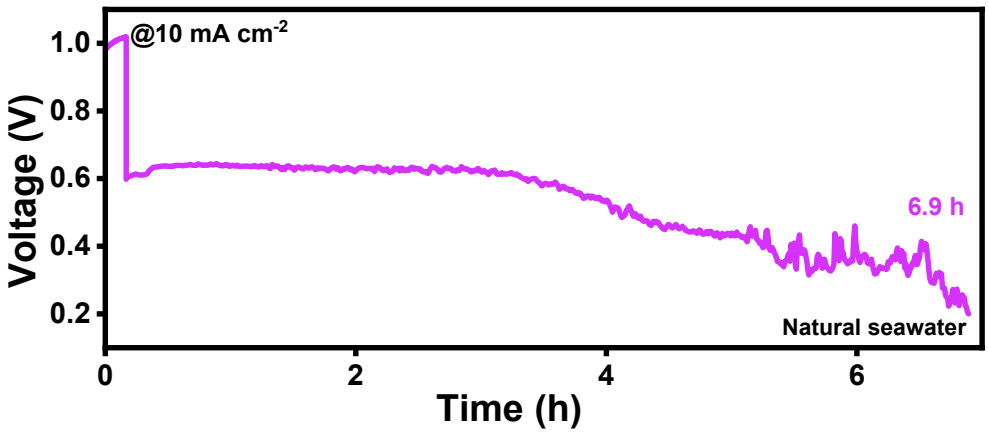

Figure S11. Discharging curve of CrN/CNS-800-based ZABs in natural seawater at 10 mA cm^{-2}.

3 Tables

Table S1. Comparable list of our catalyst against representative M-N-C materials measured in acidic solution at the rotation speed of 1600 rpm.

Catalyst	Electrolyte	Half-wave potential (V vs. RHE)	Reference
ISAS-Co/HNCS	0.5 M H_2SO_4	0.773	[1]
ISAS-Co/SNCS	0.5 M H_2SO_4	0.708	[1]
Co-N/CNFs	0.1 M $HClO_4$	0.70	[2]
C-FeZIF-1.44-950	0.1 M $HClO_4$	0.78	[3]
Cr/N/C-950	0.1 M $HClO_4$	0.761	[4]
Zn-N-C-1	0.1 M $HClO_4$	0.746	[5]
Fe/NC-NaCl	0.1 M $HClO_4$	0.832	[6]
CrN/CNS-800	**0.1 M $HClO_4$**	**0.76**	**This work**

Table S2. ORR stability list of representative transition metal nitrides measured in acidic solution.

Samples	Acidic medium	Stability at E (V vs.RHE)	Time (s)	Current retention (%)	Reference
Co_2Mo_1Nx/TiN-6	0.5 M H_2SO_4	0.2	18000	80.8%	[7]
MoN	0.1 M $HClO_4$	0.3	18000	55%	[8]
Ni_xN	0.1 M $HClO_4$	0.15	18000	50%	[9]
CoN–NGA	0.5 M H_2SO_4	0.2	40000	50%	[10]
CrN/G-carbon	0.1 M $HClO_4$	0.637	40000	52.7%	[11]
$Ti_{0.95}Ni_{0.05}N$	0.1 M $HClO_4$	0.7	30000	86.5%	[12]
$Cr_{10}Fe_2$/Z8C	0.1 M $HClO_4$	0.7	40000	57.6%	[13]
CrN@NG-900	0.5 M H_2SO_4	0.81	80000	86.2%	[14]
CrN/CNS-800	**0.1 M $HClO_4$**	**0.7**	**40000**	**81%**	**This work**

Table S3. Atomic contents of CrN/CNS-750, CrN/CNS-800 and CrN/CNS-850 in XPS analysis.

Sample	Atomic%			
	C	N	O	Cr
CrN/CNS-750	63.02	12.97	16.33	**5.71**
CrN/CNS-800	64.51	13.02	15.87	**5.04**
CrN/CNS-850	76.94	10.8	9.33	**1.66**

Table S4. List of ZABs performance in simulated/natural seawater.

Catalysts	Electrolyte	Maximum power density	Stability	Reference
Fe-N_x/NAC	2 M NH_4Cl + 1 M KCl	10.4 mW cm^{-2}	40 h（1 mA cm^{-2} ）	[15]
CrN/CNS-800	**0.5 M NaCl**	**9.7 mW cm^{-2}**	**80 h （1 mA cm^{-2} ）**	**This work**
CrN/CNS-800	**Natural seawater**	**7.3 mW cm^{-2}**	**200 h （1 mA cm^{-2} ）**	**This work**

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