

Supporting Information

Planar All-solid-state Rechargeable Zn-air Batteries for Compact Wearable Energy Storage

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Experimental section

Preparation of core-shell-structured Fe/Fe₃C@N-doped-carbon nanorod-clusters electrocatalyst. Typically, 0.2 g of ammonium iron sulfate and 1.0 g of dopamine hydrochloride were firstly added into a mixed solution consisting of 40.0 mL ethanol and 40.0 mL deionized (DI) water under vigorous stirring. Then, 4.5 mL of aqueous ammonia (25~28 wt % NH₃) was further added into the above mixture. Subsequently, the precipitate was centrifuged and washed for several times with ethanol and DI water. Then the Fe-precursor was obtained through freeze-drying of the precipitate. After that, the core-shell-structured Fe/Fe₃C@N-doped-carbon nanorod-clusters (denoted as Fe/Fe₃C@NdC-NCs) electrocatalyst can be prepared via further carbonization (heating-up to a temperature of 900 °C with a ramp of 5 °C min⁻¹ in N₂ atmosphere and keeping for 2 h) of the as-obtained Fe-precursor. For comparison, the N-doped graphitized carbon without Fe/Fe₃C core species labeled as NGC catalyst was also prepared using the same procedure only without addition of ammonium iron sulfate (Figure S2).

Fabrication and test of liquid rechargeable Zn-air batteries. Zn-air battery (ZAB) test was conducted via a home-made battery device (Figure S7a) assembled with Zn-plate served as the anode and catalyst-coated carbon cloth (1 cm²) served as the air electrode. Typically, 8 mg of catalyst was fully dispersed in a solvent consisting of 740 μL DI water, 200 μL isopropanol, and 60 μL Nafion solution (5 wt%) by sonication for 1.5 h. Then, 125 μL as-prepared catalyst ink was coated on 1 cm² carbon cloth to achieve

a catalyst loading amount of 1 mg cm^{-2} . A 6 M KOH solution containing 0.2 M $\text{Zn}(\text{CH}_2\text{COO})_2$ was employed as liquid electrolyte. ZAB tests were carried out with LAND Battery Testing System (LAND-CT2001A, China). Both the discharge/charge current and corresponding power densities were normalized to the effective area of air cathode electrode.

The specific capacity was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours}}{\text{weight of consumed zinc}}$$

The energy density was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours} \times \text{average discharge voltage}}{\text{weight of consumed zinc}}$$

The insufficient energy density was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours} \times \text{average discharge voltage}}{\text{area of device}}$$

The volumetric energy density was calculated according to the equation:

$$\frac{\text{current} \times \text{service hours} \times \text{average discharge voltage}}{\text{volume of device}}$$

Synthesis of poly(acrylamide-co-acrylic acid) solid polymer alkaline electrolyte. Typically, 4.5g acrylamide (AM, AR grade, Aladdin) and 5 mL acrylic acid (AA, AR grade, Aladdin) were dissolved in 50 ml DI to form a clear solution. Then 0.05 g N, N'-methylenebis (acrylamide) (AR grade, Aladdin) serving as cross-linkers and 0.05 mL N, N, N', N'-tetramethylethylenediamine (CP grade, Aladdin) serving as accelerant were added subsequently. This mixture was stirred with a magnetic stirrer until the reactant was dissolved completely. After the mixture being deoxygen for 30 min with nitrogen gas, 0.01 g initiator ammonium persulfate (APS) was added and stirred rapidly for 10 s. Take the homogeneous solution (1 ml) into a cubic container ($2.0 \text{ cm} \times 2.0 \text{ cm} \times 1.0 \text{ cm}$). After heating at $60 \text{ }^\circ\text{C}$ for 3 h, poly(acrylamide-co-acrylic acid) (P-(AM-co-AA)) gel film was obtained. Finally, the as-synthesized P-(AM-co-AA) gel film was dried in a drying oven for 12 h at $80 \text{ }^\circ\text{C}$ to remove the water, and then soaked in a 20 mL mixture solution of 6 M KOH and 0.2 M $\text{Zn}(\text{CH}_2\text{COO})_2$ for 24 h to form the P-(AM-co-AA) solid polymer alkaline electrolyte. For comparison, pure polyacrylamide (PAM) and polyacrylic acid (PAA) hydrogel were also prepared using the

same procedure only without addition of AA and AM, respectively. In addition, the frequently-used polyvinyl alcohol/potassium hydroxide (PVA/1M KOH) gel electrolyte was also prepared by dissolving 1 g PVA in 10 mL water and stirred at about 90 °C for 2 h, followed by adding 2.0 mL KOH (6 mol L⁻¹) and stirring the solution till it became clear.

Figure S9 shows the Fourier-transform infrared spectrum of the as-prepared samples. The two peaks around 2923 and 3363 cm⁻¹ are assigned to the C–H stretching vibration of –CH₂ group and N–H antisymmetric stretching vibration of –NH₂ group, and the absorption band at 1587 cm⁻¹ is the characteristics of N–H bending vibration of –NH₂ group. All of them are typical absorption bands of PAM. The band at 1680 cm⁻¹ is attributed to the stretching vibration of C=O in carboxylic group, and the band at 1405 cm⁻¹ is attributed to the symmetric –COO stretching vibration in carboxylic group, which are the typical absorption bands of PAA. All of these characteristic absorption bands are observed in the as-obtained P-(AM-co-AA) gel, fully showing that the product is a copolymer of AM and AA.

Fabrication and test of planar all-solid-state Rechargeable Zn-air batteries. First, a home-made interdigital cutting-mould with customized geometric parameters was employed to fabricate finger-shaped Zn-foil (thickness of 0.03 mm) and carbon cloth as shown in FigureS8. Then the as-prepared electrocatalyst ink was coated on the finger-shaped carbon cloth (loading amount of 1 mg cm⁻²). Subsequently, the as-obtained interdigital anode/cathode electrodes were deployed on a solid P-(AM-co-AA)/6M KOH alkaline gel electrolyte film supported by a bottom silicone encapsulation layer (Ecoflex 00-30, mix ratio is 1A:1B by weight). After that, a top silicone encapsulation layer with air holes was overlaid on the well-deployed interdigital anode/cathode electrodes and adhered firmly to the bottom silicone encapsulation layer with semicured silicone serving as glue. After fully curing of the semicured silicone with thermal treatment in an oven of 50 °C for 30 min, a planar all-solid-state rechargeable Zn-air battery is successfully prepared and packaged, without peeling off.

Characterization. The microstructure and phase composition of the as-obtained samples were characterized by X-ray powder diffraction (XRD Bruker D8-ADVANCE) with an 18 kW advanced X-ray diffractometer with Cu K_α radiation (λ=1.54056Å), Raman spectroscopy (inVia-Reflex, Renishaw, UK), Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan), Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), and Fourier transform infrared spectroscopy (VERTEX 801HYPERION2000, Bruker Optics, Germany). Surface area was determined by nitrogen adsorption-desorption method at 77 K (3H-2000PS2, BeiShiDe Instrument, China). X-ray photoelectron spectroscopy (XPS) was conducted with a Mg K_α achromatic X-ray source.

Electrochemical measurement. All the oxygen reduction reaction (ORR) tests were performed on the electrochemical work station (CHI 760E, Chenhua, Shanghai) in a convention three-electrode cell equipped with a Pt wire counter electrode, an Ag/AgCl reference electrode, and a glassy carbon (GC) disk electrode. The obtained potentials are referred to the reversible hydrogen electrode (RHE), $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^0_{\text{Ag/AgCl}}$. The rotating disk electrode (RDE: Pine Research Instrument, USA) was used as the working electrode. For each sample, 5 mg catalyst was ultrasonically dispersed in a solution consisting of 700 μL DI water, 250 μL isopropanol, and 50 μL Nafion solution (5 wt%). Subsequently, the obtained homogeneous catalyst ink with a volume of 8 μL was dripped on a glassy carbon rotating disk electrode (RDE, 5 mm in diameter) and dried thoroughly at room temperature. The Pt/C catalyst (20 wt%) ink was prepared with the same procedure for comparison. In alkaline media, the RDE test was carried out at room temperature in O_2 -saturated 0.1 M KOH solution. The cyclic voltammetry (CV) measurements were scanned from -0.8 to 0 V (vs. Ag/AgCl) at a scan rate of 20 mV s^{-1} . The RDE test was carried out with linear sweep voltammetry (LSV) in a potential range of -0.8 to 0.2 V (vs. Ag/AgCl) at a scanning rate of 5 mVs^{-1} under different rotational rates from 400 to 2500 rpm in an O_2 -saturation alkaline electrolyte. Under the same condition, oxygen evolution reaction (OER) measurements were carried out by linear sweep voltammetry (LSV) at a potential range from 0 to 1.0 V (vs. Ag/AgCl) at a scan rate of 5 mVs^{-1} under 1600 rpm. Koutecky-Levich (K-L) plots were obtained from the ORR polarization curves at different potentials. The electron transfer number (n) per O_2 molecule in ORR was determined by the slopes of the linear fit lines on the basis of the following Koutecky-Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B \times \omega^{1/2}}$$

$$B = 0.2 \times n \times F \times C_{\text{O}_2} \times D_{\text{O}_2}^{2/3} \times \nu^{-1/6}$$

where j is the measured current density, j_k is the kinetic current density, ω is the electrode rotation rate, F is the Faradic constant (96485 C mol^{-1}), C_{O_2} is the saturated oxygen concentration in 0.1 M KOH aqueous solution ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$), D_{O_2} is the oxygen diffusion coefficient ($1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), ν is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$) and n is the electron transfer number in ORR. Rotating ring-disk electrode (RRDE: Pine Research Instrument, USA) voltammogram measurements for the calculation of the ORR electron transfer number were conducted on an RRDE configuration with a 320 μm gap Pt ring electrode. The electron transfer numbers (n) and peroxide yield (HO_2^- %) can be obtained from the RRDE curve using the Eqs, respectively.

$$n = 4 \times \frac{I_d}{I_d + I_r/N}$$

$$\text{HO}_2^- \% = 200 \frac{I_r/N}{I_d + I_r/N}$$

where I_d is the disk current, I_r is the ring current and N is the current collection efficiency of the Pt ring which was determined to be 0.37. The stability of the catalyst was examined through CV scanning of 10000 cycles (300 mV s^{-1}). Electrochemical impedance spectroscopy (EIS) measurements were evaluated with the frequency range from 100 kHz to 0.01 Hz.

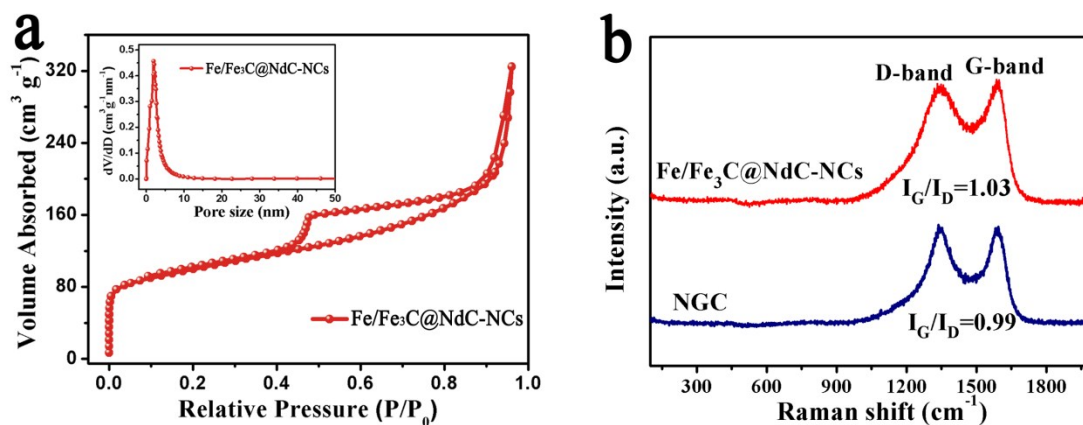


Figure S1. a) N_2 adsorption-desorption isotherms and BJH pore-size distribution of the Fe/Fe₃C@NdC-NCs; b) Raman spectra of the NGC and Fe/Fe₃C@NdC-NCs catalysts.

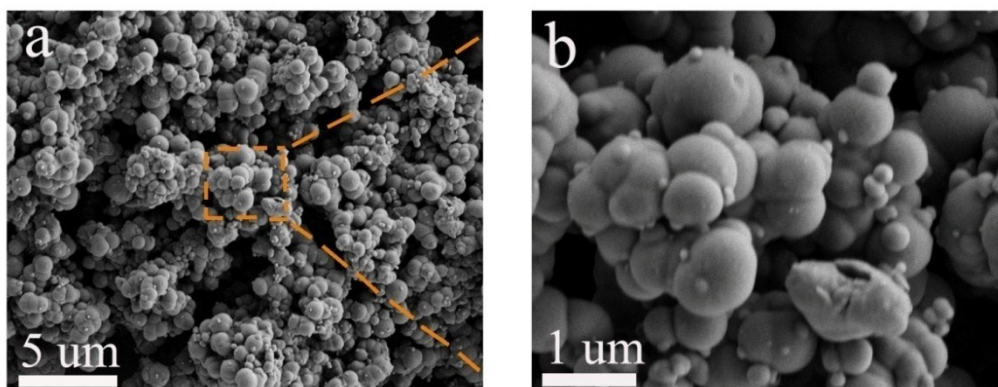


Figure S2. a) Low-magnification and b) High-magnification SEM images of NGC.

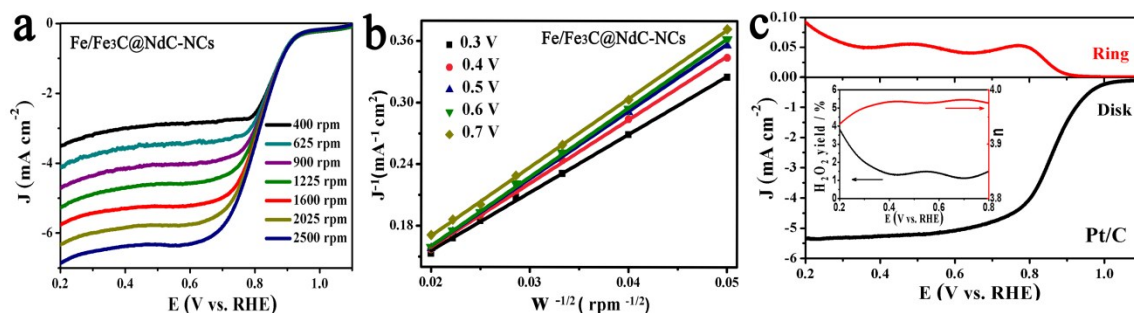


Figure S3. a) LSVs for the ORR, and b) corresponding K-L plots of Fe/Fe₃C@NdC-NCs catalyst at different rotating rates; c) Peroxide yield and electron transfer number for the Pt/C catalyst obtained from RRDE voltammograms at a rotating rate of 1600 rpm in O₂-saturated 0.1 M KOH.

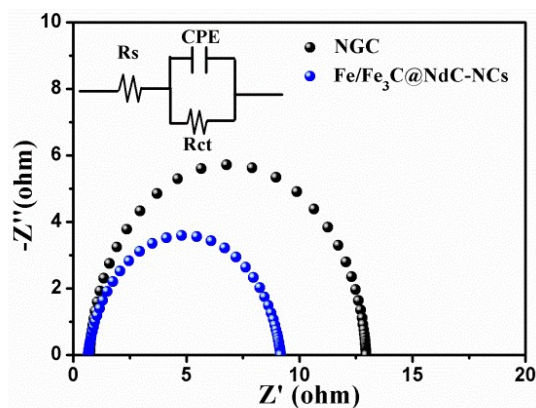


Figure S4. Electrochemical impedance spectra (EIS) of the NGC and Fe/Fe₃C@NdC-NCs catalysts obtained in 0.1 M KOH and corresponding equivalent circuit.

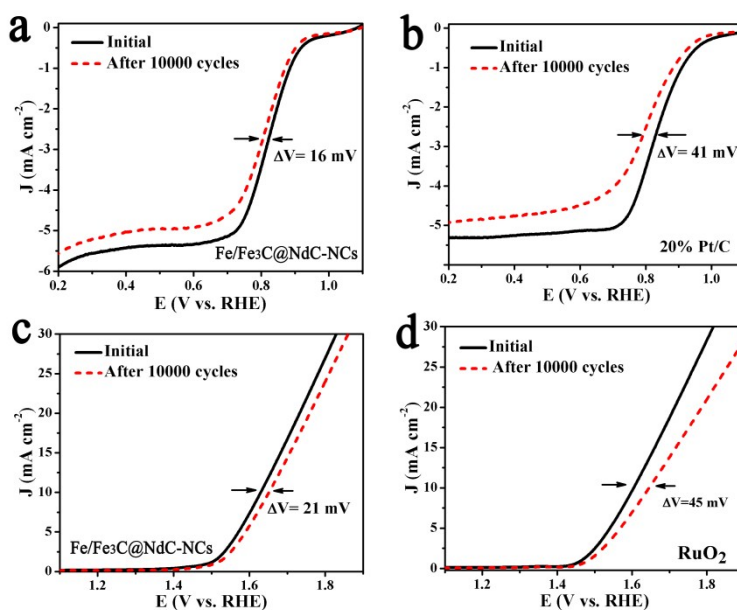


Figure S5. Polarization curves of the a, c) Fe/Fe₃C@NdC-NCs catalyst, and b, d) commercial 20% Pt/C and

RuO₂ catalysts before and after 10000 cycles in an O₂/N₂-saturated 0.1 M KOH solution.

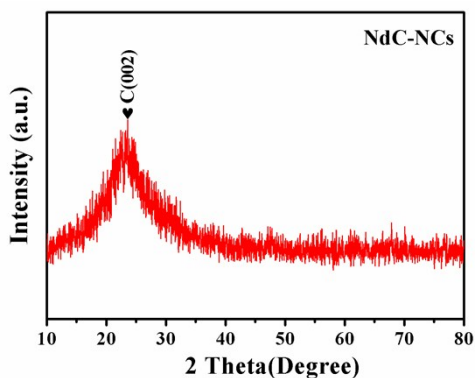


Figure S6. The XRD pattern of the NdC-NCs contrast sample with acid to remove Fe/Fe₃C core species.

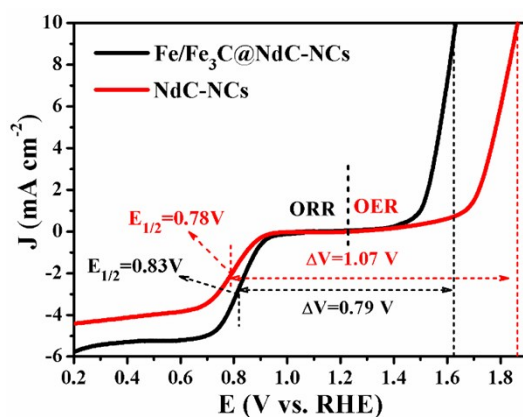


Figure S7. The overall LSV curves of the Fe/Fe₃C@NdC-NCs and NdC-NCs contrast sample with acid to remove Fe/Fe₃C core species in the whole ORR and OER region in 0.1 M KOH.

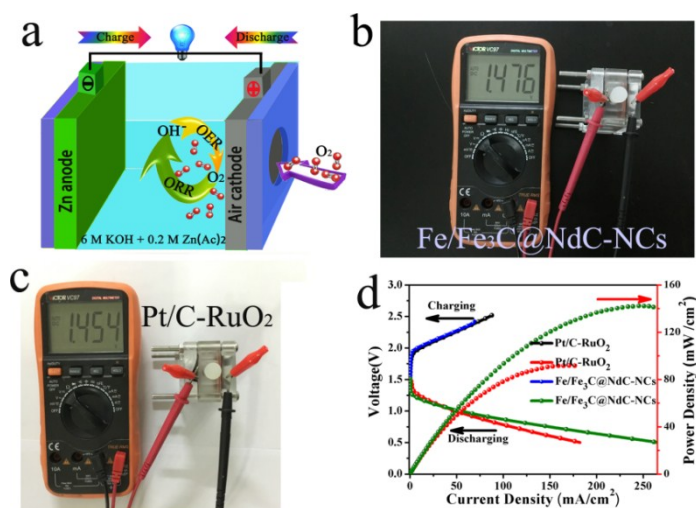


Figure S8. a) Schematic of a home-made liquid ZAB device; Open-circuit-potential of the liquid ZAB equipped with b) Fe/Fe₃C@NdC-NCs catalyst and c) Pt/C-RuO₂ mixed catalysts; d) Charge and discharge polarization curves of the fabricated liquid ZABs.

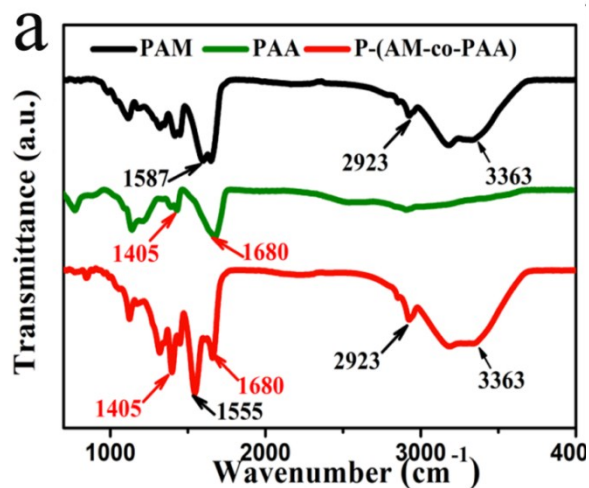


Figure S9. FTIR spectra of PAM, PAA and P-(AM-co-AA) gel.

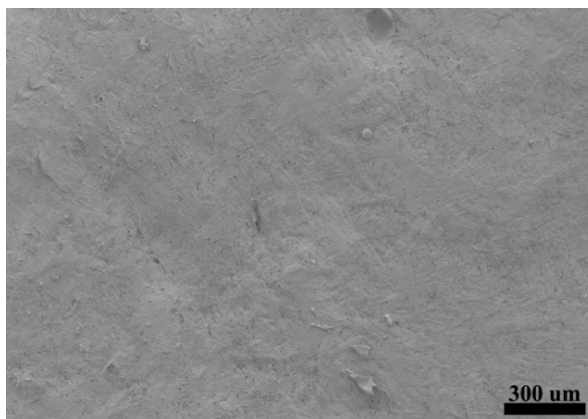


Figure S10. A typical SEM image of cross-section of PVA gel after freeze-drying procedure.

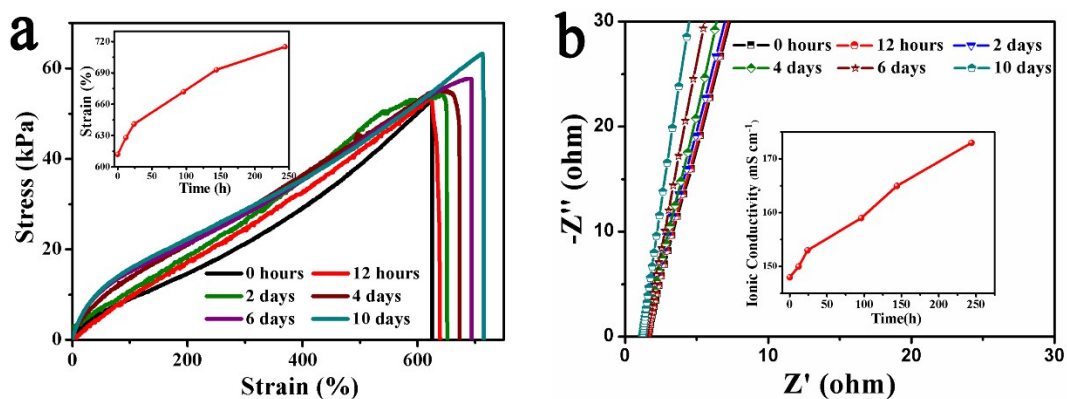


Figure S11. a) The corresponding tensile stress-strain curves of P-(AM-co-AA)/6 M KOH alkaline gels after total exposure without cover to air for different time; b) AC impedance spectrum at 0.1 V over the frequency range from 100000 to 0.01 Hz for P-(AM-co-AA)/6M KOH alkaline gels after total exposure without cover to air for different time.

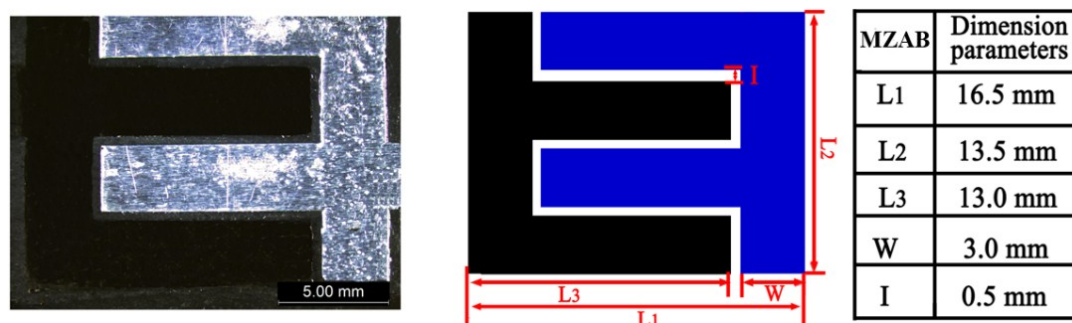


Figure S12. Typical optical microscope photograph of the symmetrical interdigital electrodes of a single PAR-ZAB unit, and actual geometric parameters.

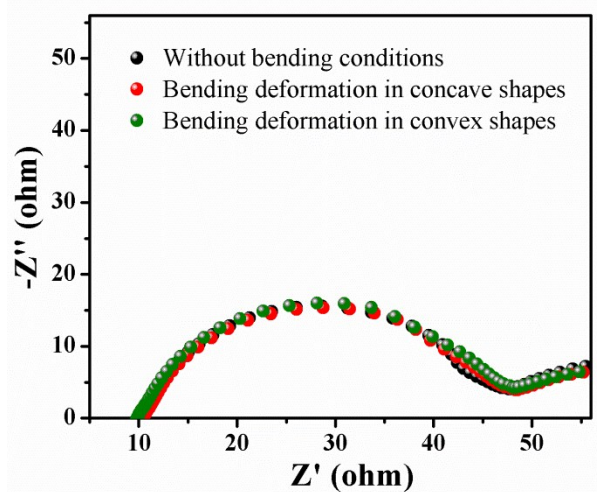


Figure S13. The Nyquist plots of tandem cell in unbending and bending states.

Table S1. List of the ORR/OER catalytic properties of currently reported state-of-the-art bifunctional catalysts, and our demonstrated Fe/Fe₃C@NdC-NCs bifunctional catalyst in 0.1 M KOH.

Catalyst	Electrolyte	ORR, E _{onset} /V	ORR, E _{1/2} /V	J _L (mA cm ⁻²)	OER, E _(j=10) /V	ΔE=E _(j=10) -E _{1/2} /V	Ref.
Fe/Fe ₃ C@Nd C-NCs	0.1 M KOH	0.92	0.83	5.91	1.62	0.79	This work
CoFe/N-GCT	0.1 M KOH	0.91	0.79	4.86	1.67	0.88	Angew. Chem. Int. Ed. 2018, 57, 16166.
NC@Co- NGC	0.1 M KOH	0.92	0.82	5.3	1.64	0.82	Adv. Mater. 2017, 29, 1700874.
Co-N,B-CSs	0.1 M KOH	0.89	0.83	5.66	1.66	0.83	ACS Nano 2018, 12, 1894.
Co ₃ FeS _{1.5} (O H) ₆	0.1 M KOH	N. A.	0.721	N. A.	1.588	0.867	Adv. Mater. 2017, 29, 1702327
Co ₂ P/CoNi _n NCNTs	0.1M KOH	0.96	0.85	5.01	1.65	0.80	Adv. Funct. Mater. 2018, 1805641.
NiCo/PFC	0.1 M KOH	0.92	0.79	5.61	1.62	0.83	Nano Lett. 2016, 16, 6516.
CoZn-NC700	0.1 M KOH	0.98	0.84	4.93	1.63	0.89	Adv. Funct. Mater. 2017, 27, 1700795.
Fe@CNG/N CNTs	0.1 M KOH	0.93	0.84	5.00	1.68	0.84	J. Mater. Chem. A 2018,6, 516.
CoNCF- 1000-80	0.1 M KOH	0.92	0.82	5.03	1.66	0.84	Small 2018, 14, 1703739.