# Supporting Information

## Monolithic Heteronanomat Paper Air Cathodes Toward Origami-Foldable/Rechargeable Zn-Air Batteries

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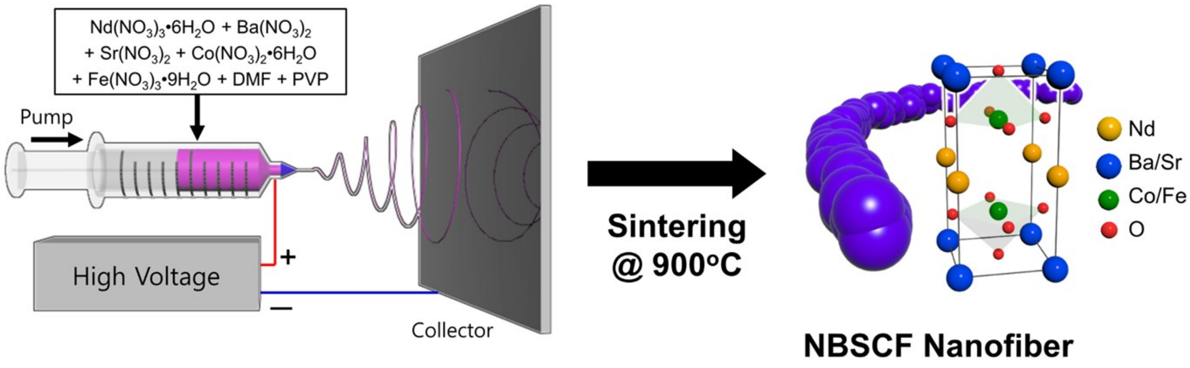



**Figure S1.** Schematic illustration of the synthetic procedure of NBSCF nanofibers by electrospinning.

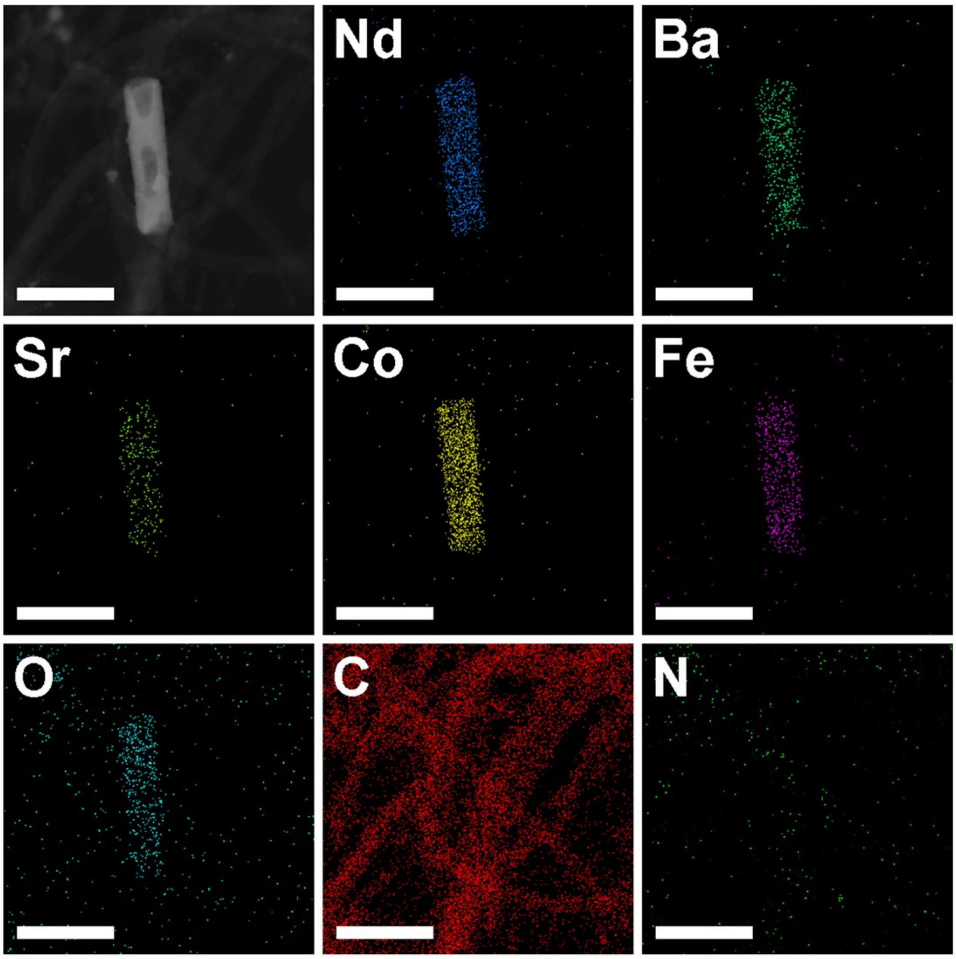



**Figure S2.** HAADF-TEM and EDS elemental mapping images of the N-CNT/NBSCF mixture; scale bar 500 nm.

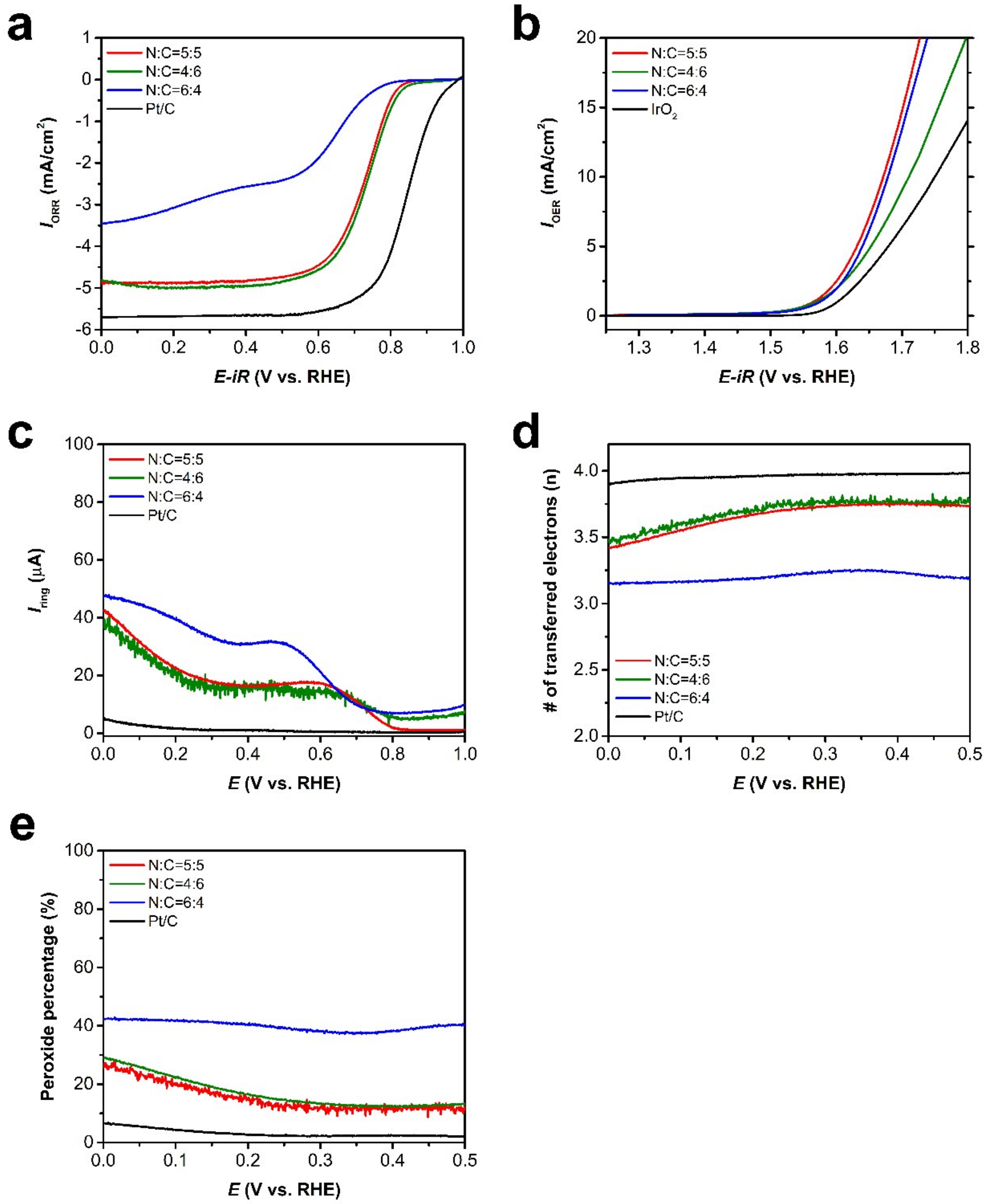



**Figure S3.** (a) ORR and (b) OER results of the NBSCF/N-CNT mixture with various ratios in 0.1 M KOH solution at 1600 rpm with a scan rate of 10 mV $s^{-1}$. (c) Ring current, (d) number of transferred electrons, and (e) peroxide percentage of ORR.

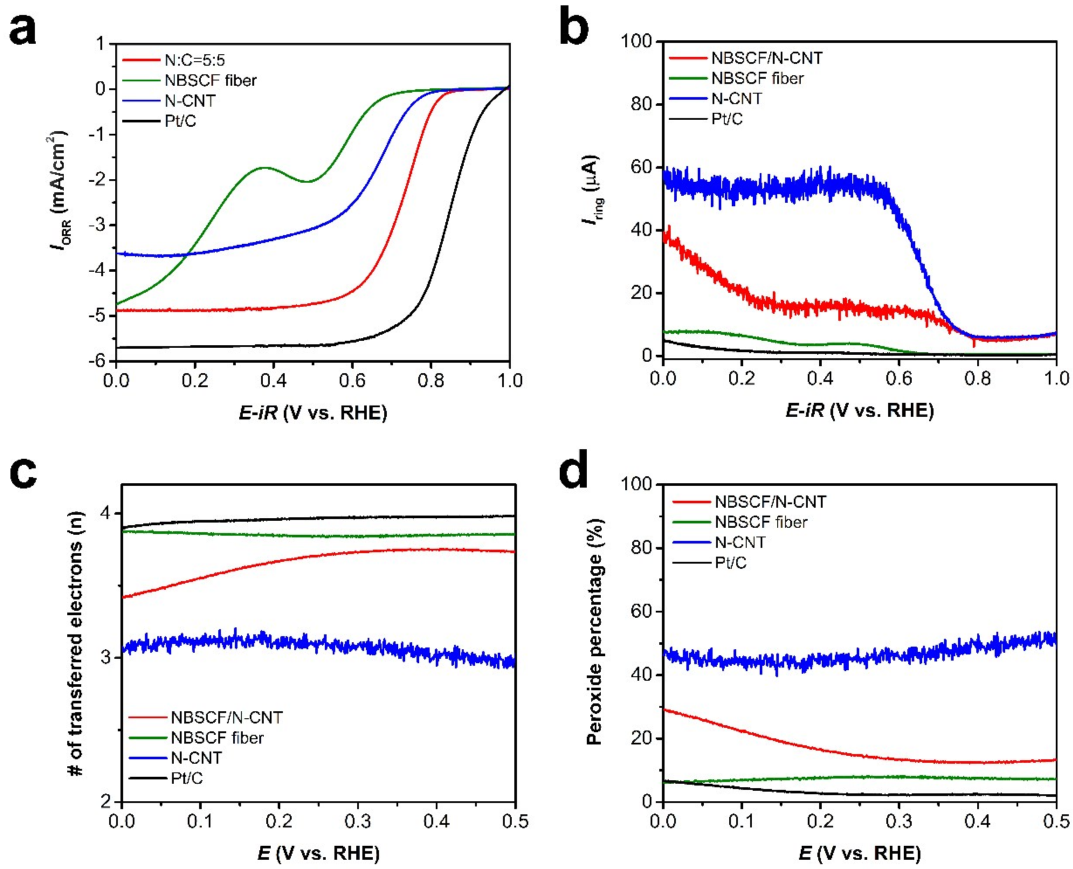



**Figure S4.** (a) Disc current, (b) ring current, (c) number of transferred electrons, and (d) peroxide percentage of the NBSCF/N-CNT mixture with NBSCF fiber, N-CNT, and Pt/C for comparison in 0.1 M KOH solution at 1600 rpm with a scan rate of 10 mV $s^{-1}$.

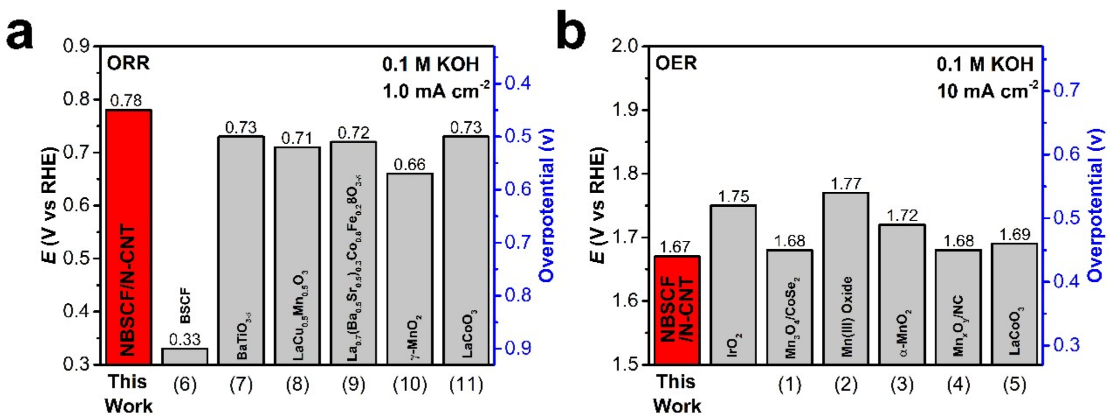



**Figure S5.** (a) ORR and (b) OER performance of the recently reported non-perovskite and perovskite electrocatalysts in alkaline solution (0.1 M KOH).

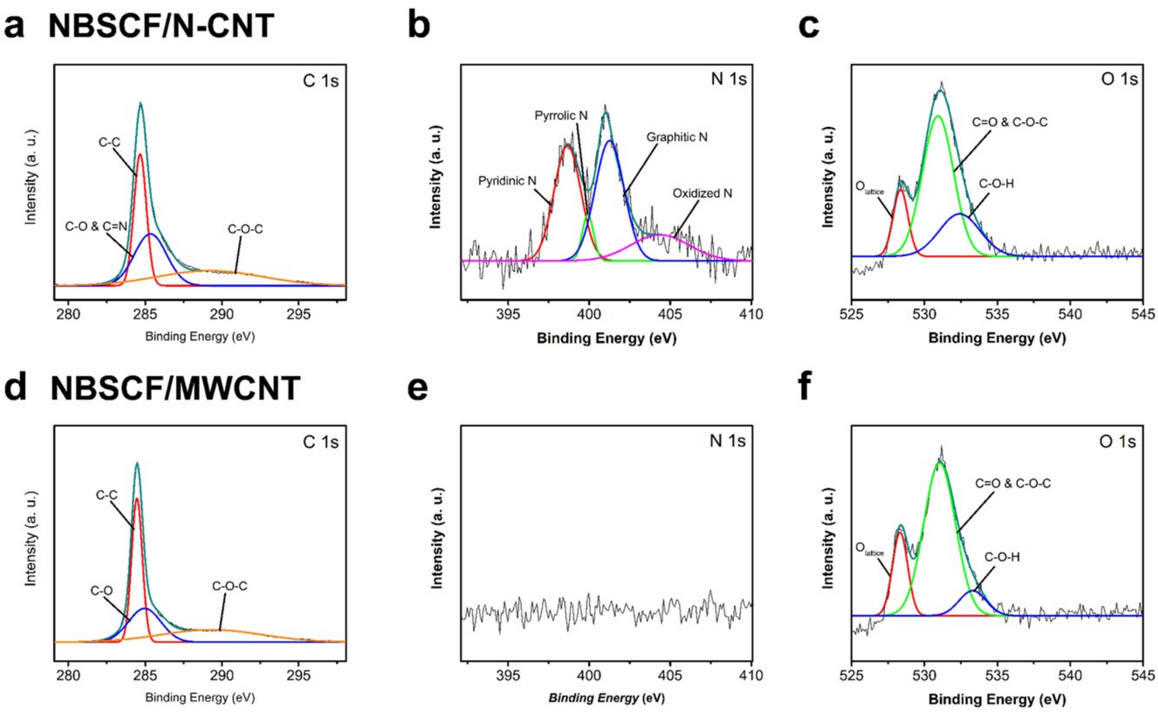



**Figure S6.** XPS spectra of (a), (d) Carbon 1s orbital, (b), (e) Nitrogen 1s orbital, and (c), (f) Oxygen 1s orbital of the NBSCF/N-CNT mixture and NBSCF/MWCNT mixture (control sample).

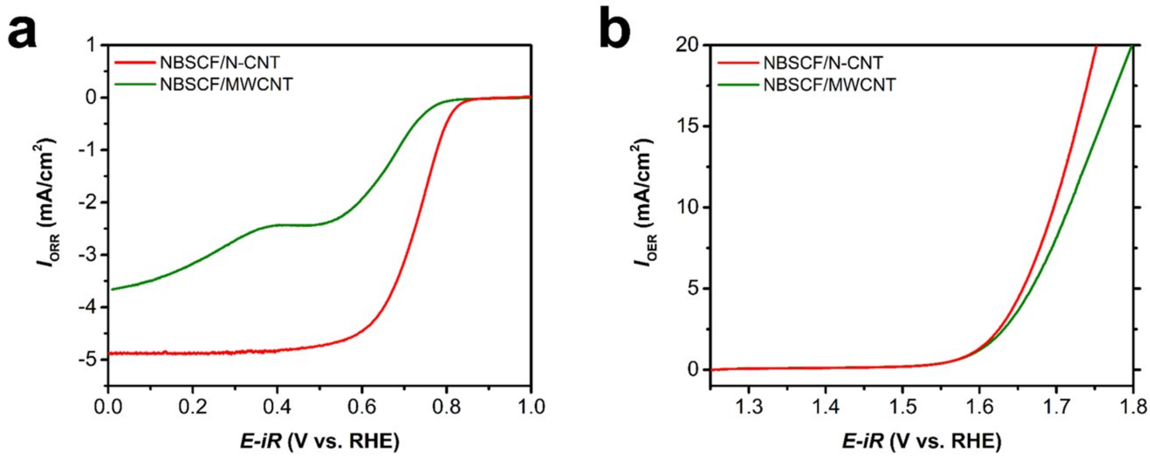



**Figure S7.** (a) ORR and (b) OER performance of the NBSCF/N-CNT mixture and NBSCF/MWCNT mixture (control sample).

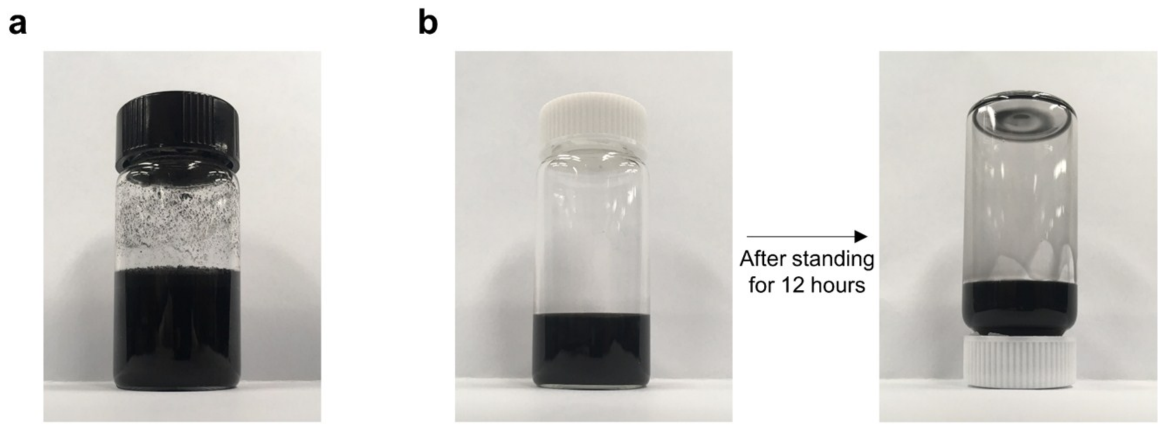



**Figure S8.** Photographs showing dispersion stability of the cathode suspension: (a) without and (b) with a dispersion agent (SDS/urea = 5/5 (w/w)).

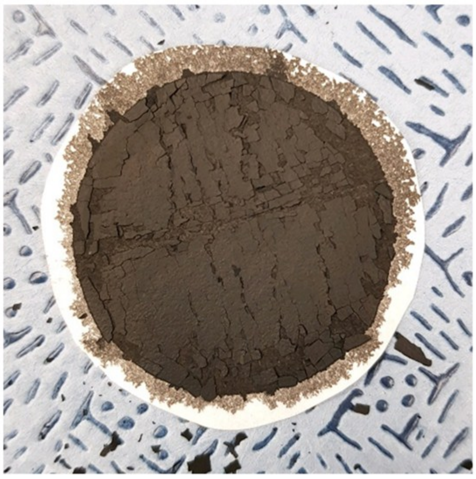


**Figure S9.** Photograph of the MH paper air cathode without CNFs.

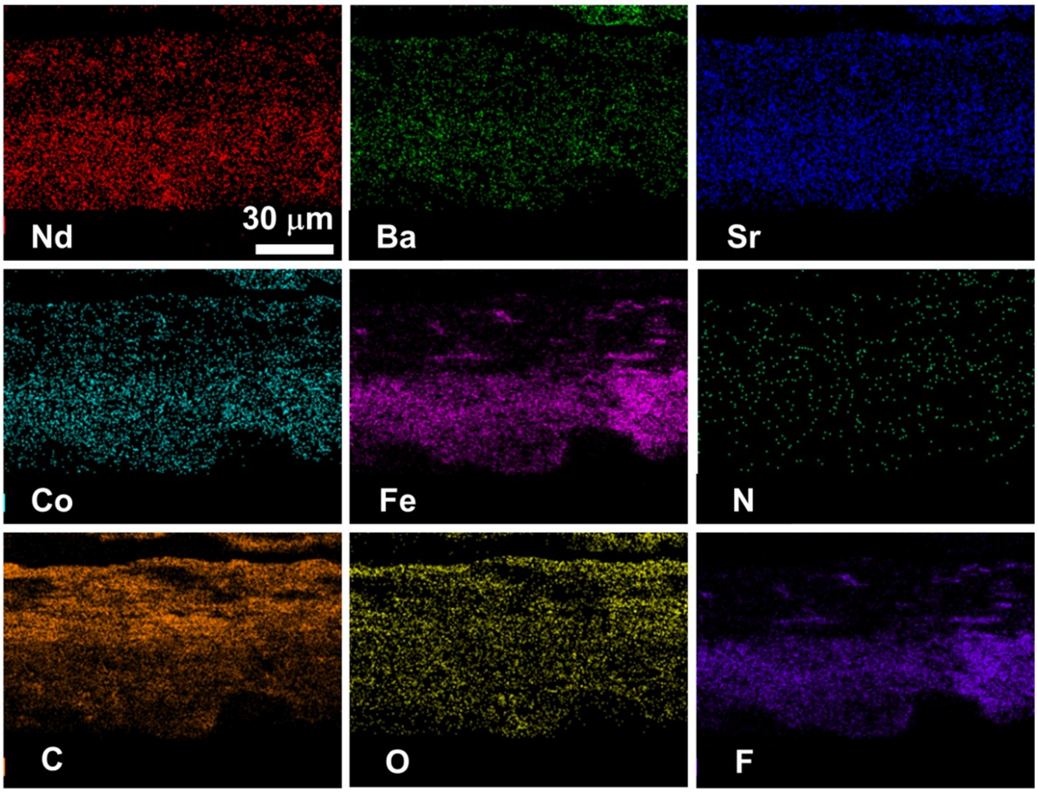
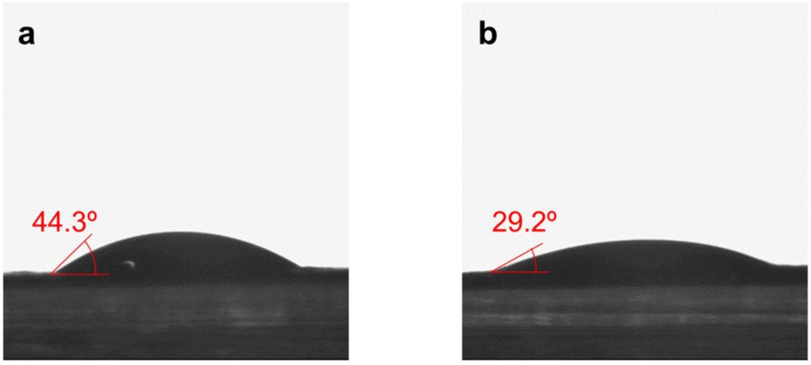



**Figure S10.** Cross-sectional EDS mapping images (Nd, Ba, Sr, Co, Fe, N, C, O, and F elements are represented by the colored dots) of the MH paper air cathode.




Paper air cathode with 14 wt% of CNF    Paper air cathode with 40 wt% of CNF

**Figure S11.** Photographs showing the water contact angle of the MH paper air cathodes with: (a) 14 wt% CNF and (b) 40 wt% CNF.

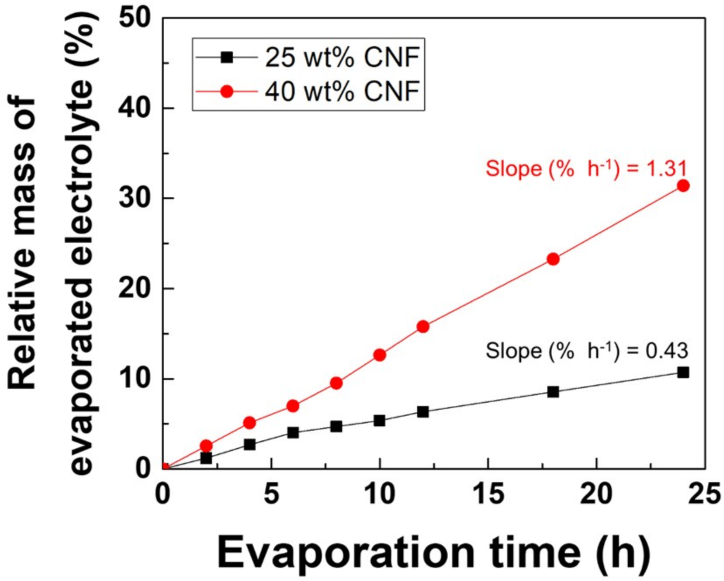



**Figure S12.** Change in electrolyte content (expressed by relative mass of evaporated electrolyte) of the MH paper air cathode during the evaporation test (*i.e.*, exposure to ambient condition).

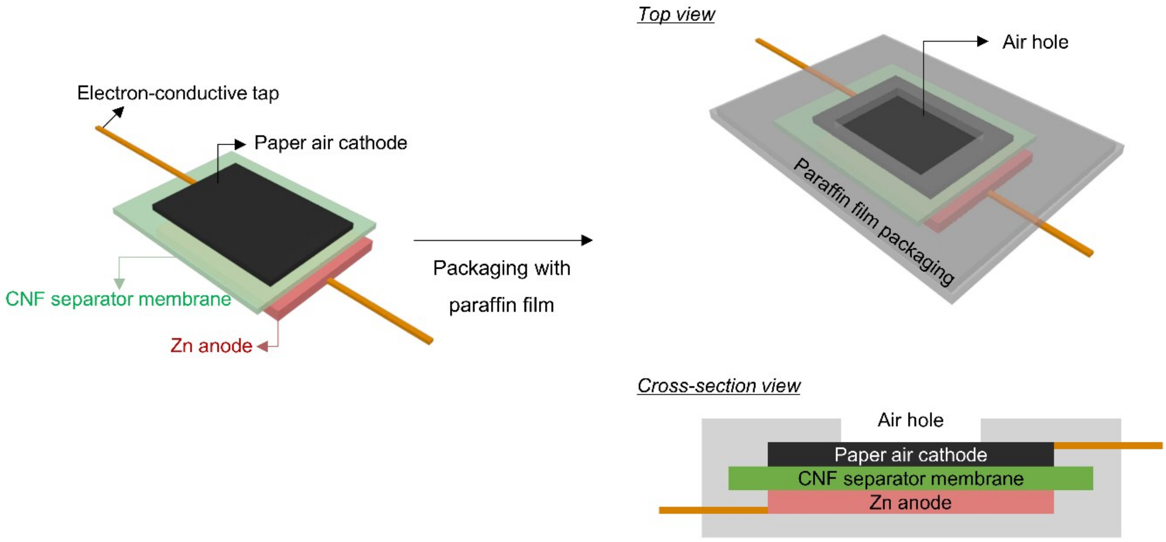



**Figure S13.** Schematic representation showing the assembly of the pouch-type Zn-air battery. The Zn-air battery was composed of MH paper air cathode, alkaline electrolyte-soaked CNF separator membrane, and Zn foil anode. The cell components were finally sealed with a paraffin film with holes that allow air passage.

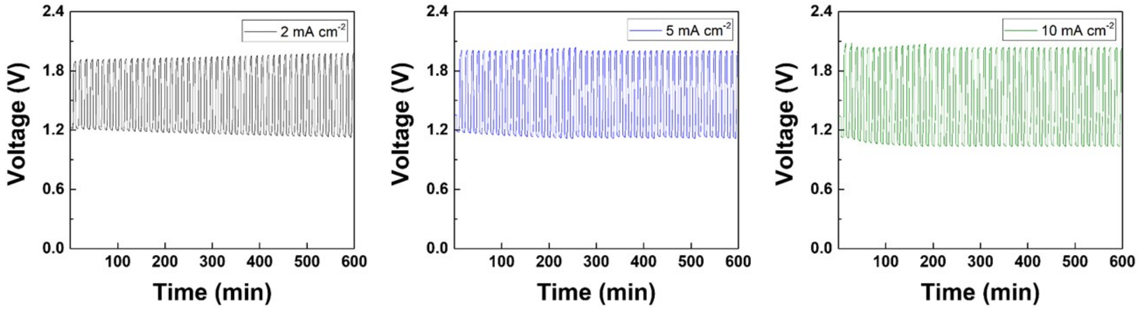



**Figure S14.** The results of cycling performance of the foldable Zn-air battery at a current density range of 2 − 10 mA cm$^{-2}$.

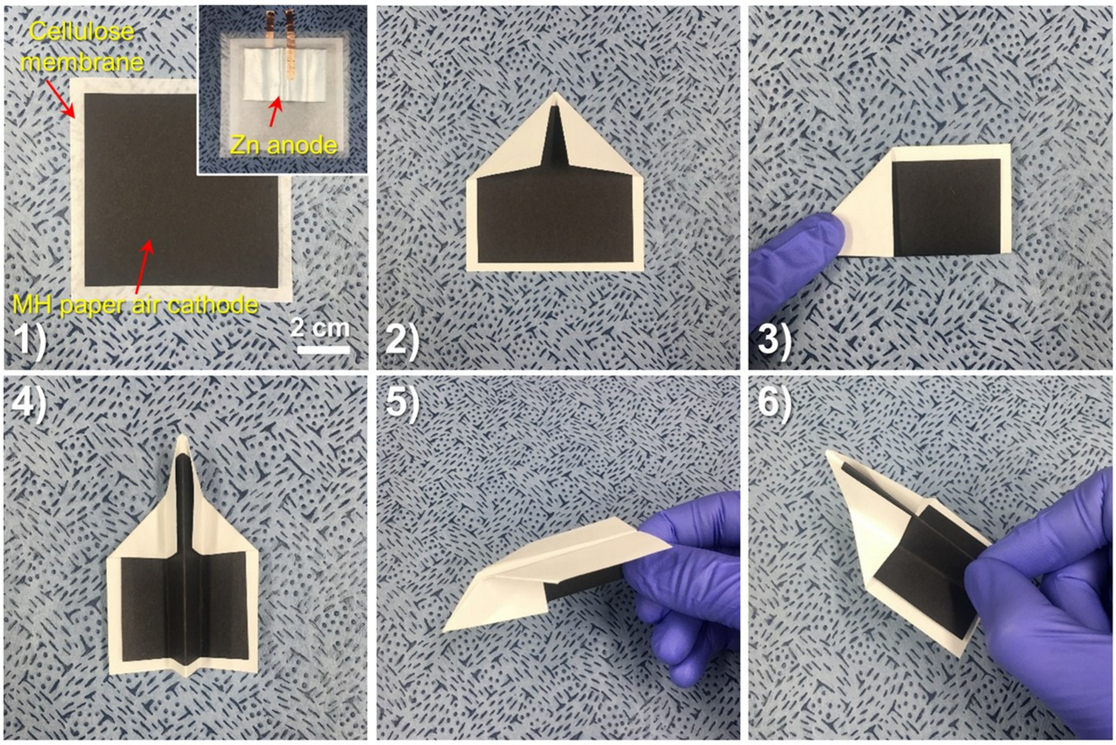



**Figure S15.** Photographs depicting origami folding-based stepwise fabrication procedure of the paper airplane-shaped Zn-air battery.

**Table S1.** Comparison of ORR performance of this study with the previously reported non-perovskite/perovskite electrocatalysts in alkaline solution (KOH).

| Publication | Catalysts | Electrolyte (M) | Electrode | J (mA cm$^{-2}$) | E (V vs RHE) | $J_{0.6V}$ (mA cm$^{-1}$) |
|---|---|---|---|---|---|---|
| This work | NBSCF/N-CNT | 0.1 | RRDE | 1 | 0.78 | 4.46 |
| This work | NBSCF | 0.1 | RRDE | 1 | 0.56 | 0.93 |
| This work | N-CNT | 0.1 | RRDE | 1 | 0.70 | 2.53 |
| This work | Pt/C | 0.1 | RRDE | 1 | 0.90 | 4.73 |
| *ACS. Catal*. **2014**, *4*, 1061 | $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | 0.1 | RRDE | 1 | 0.33 | 0.0046 |
| *J. Am. Chem. Soc*. **2016**, *138*, 3541 | $BaTiO_{3-x}$ | 0.1 | RDE | 1 | ~0.73 | ~2 |
| *Nat. Chem*. **2011**, *3*, 546 | $LaCu_{0.5}Mn_{0.5}O_3$ | 0.1 | RDE | 1 | ~0.71 | ~4.10 |
| *Energy Environ. Sci*. **2016**, *9*, 176 | $La_{0.7}(Ba_{0.5}Sr_{0.5})_{0.3}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | 0.1 | RRDE | 1 | ~0.72 | |
| *Chem. Mater*. **2010**, *22*, 898 | $\gamma$-$MnO_2$ | 0.1 | RDE | 1 | ~0.66 | ~1.10 |
| *ACS Nano*, **2017**, 11, 11594 | PBSCF-NF | 0.1 | RRDE | 1 | 0.73 | 4.13 |

**Table S2.** Comparison of OER performance of this study with the previously reported non-perovskite/perovskite electrocatalysts in alkaline solution (KOH).

| **Publication** | **Catalysts** | **Electrolyte (M)** | **Electrode** | **J (mA cm$^{-2}$)** | **E (V vs RHE)** | **Overpotential (V)** |
|---|---|---|---|---|---|---|
| This work | NBSCF/N-CNT | 0.1 | GC | 10 | 1.67 | 0.44 |
| This work | NBSCF | 0.1 | GC | 10 | 1.63 | 0.40 |
| This work | N-CNT | 0.1 | GC | 10 | - | - |
| This work | $IrO_2$ | 0.1 | GC | 10 | 1.75 | 0.52 |
| *J. Am. Chem. Soc.* **2012**, *134*, 3517 | $Mn_3O_4/CoSe_2$ | 0.1 | GC | 10 | 1.68 | 0.45 |
| *J. Am. Chem. Soc.* **2010**, *132*, 13612-13614 | $MnO_x$ thin film | 0.1 | GC | 10 | 1.77 | 0.54 |
| *J. Am. Chem. Soc.* **2013**, *135*, 8452 | α-$MnO_2$-SF | 0.1 | Graphite carbon | 10 | 1.72 | 0.49 |
| *Angew. Chem. Int. Ed.* **2014**, *53*, 7584 | $Mn_xO_y$/NC | 0.1 | GC | 10 | 1.68 | 0.45 |
| *Science*. **2011**, *334,* 1383 | $LaCoO_3$ | 0.1 | GC | 2 | ~1.69 | 0.46 |

**Table S3.** Comparison of mechanical flexibility and electrochemical performances of the Zn-air batteries (this study vs. previous studies).

| Publication | Electrode components | | Electrolyte | Mechanical flexibility | | OCV | Energy density | Power density | Cycle performance |
|---|---|---|---|---|---|---|---|---|---|
| | Anode | Cathode | | Deformation mode | Operating voltage | | | | |
| **This work** | Zn foil | NBSCF, N-CNT, CNF, PTFE | Nanocellulose membrane /KOH | Multiple-folded paper airplane | Disch. ~ 1.22 V Ch. ~ 1.92 V (at 1 mA $cm^{-2}$) | 1.44 V | 6.48 mWh $cm^{-2}$ (at 1 mA $cm^{-2}$) | 18.59 mW $cm^{-2}$ (at 20 mA $cm^{-2}$) | > 75 cycles (at 1 mA $cm^{-2}$, 1.2 – 1.9 V) |
| *Adv. Mater.* **2016**, *28*, 3000 | Zn foil | Carbon nanofiber | PVA gelled electrolyte | Bending (Not quantitatively estimated) | Disch. ~ 1.0 V Ch. = 1.78 V (at 2 mA $cm^{-2}$) | 1.26 V | 378 Wh $kg^{-1}$ (at 2 mA $cm^{-2}$) | ~ 2 mW $cm^{-2}$ (at 2 mA $cm^{-2}$) | Not provided for the flexible cell |
| *J. Am. Chem, Soc.* **2016**, *138*, 10226 | Zn belt | $Co_4N$/carbon network/carbon cloth | PVA/KOH | Bending (0, 30, 60, 90, 120°) | Disch. ~ 1.2 V (at 0.5 mA $cm^{-2}$) | 1.35 V | ~ 9.76 mWh $cm^{-2}$ (at 0.5 mA $cm^{-2}$) | ~ 0.6 mW $cm^{-2}$ (at 0.5 mA $cm^{-2}$) | 36 cycles (at 0.5 mA $cm^{-2}$, 1.19 – 1.96 V) |
| *Adv. Energy Mater.* **2017**, *7* 1700779 | Zn film | $Co_3O_4$/carbon cloth | PVA/KOH | Bending (bending radius = 51, 28, 13 mm) (integrated with a flexible display) | Disch. ~ 1.04 V Ch. ~ 1.94 V (at 2.0 mA $cm^{-2}$) | 1.33 V | ~ 546 Wh $kg^{-1}$ (at 2 mA $cm^{-2}$) | ~ 2.1 mW $cm^{-2}$ (at 2 mA $cm^{-2}$) | 30 cycles (at 2 mA $cm^{-2}$, 1.02 – 1.97 V) |
| *Adv. Energy Mater.* **2017**, *7*, 1700927 | Zn foil | $MnO_2$ grown on graphene-coated carbon cloth | Crosslinked polyacrylic acid-based electrolyte | Bending (OCV, EIS) ex-situ folding (10, 50, 100 times) | Disch. ~ 1.29 V Ch. ~ 1.94 V (at 1.0 mA $cm^{-2}$) | 1.4 V | - | ~ 32 mW $cm^{-2}$ (at approx. 52 mA $cm^{-2}$) | 175 cycles (at 0.7 mA $cm^{-2}$, 1.3 – 1.9 V) |
| *Adv. Mater.* **2017**, *29*, 1602868 | Electrodeposited Zn on carbon cloth | N-doped $Co_3O_4$/carbon cloth | PVA gelled electrolyte | Bending (Not quantitatively estimated) | - | 1.1 V | ~ 644 Wh $kg^{-1}$ (at 2.5 mA $cm^{-3}$) | - | - |
| *Adv. Energy Mater.* **2018**, *8* 1800612 | Zn foil | Sulfur-modified $CaMnO_3$/carbon cloth | PVA gelled electrolyte | Bending (0, 30, 60, 90, 120, 150°) | Disch. ~ 0.83 V Ch. ~ 1.83 V (at 1 mA $cm^{-2}$) | 1.32 V | - | ~ 3.3 mW $cm^{-2}$ (at 3 mA $cm^{-2}$) | > 10 hours (~ 20 cycles) (at 1 mA $cm^{-2}$, 1.15 – 1.83 V) |
| *Energy Environ. Sci.* **2018**, *11*, 1723 | Zn foil | Porphyrin COF, conductive carbon, PTFE, Nafion | PVA gelled electrolyte | Bending (0, 30, 90, 150, 180°) | Disch. ~ 1.22 V Ch. ~ 1.98 V (at 1 mA $cm^{-2}$) | 1.39 V | - | 22.3 mW $cm^{-2}$ (at ~ 30 mA $cm^{-1}$) | Not provided for the flexible cell |
| *Adv. Mater.* **2019**, 1807468 | Zn foil | 1 nm-$CoO_x$/ N-RGO/ Nafion/carbon cloth | PVA gelled electrolyte | Bending (0, 90, 180°) | Disch. ~ 1.25 V Ch. ~ 1.82 V (at 6 mA $cm^{-2}$) | 1.39 V | - | 600 W $g^{-1}$ (at 200 mA $cm^{-2}$) | > 10 hours (~ 60 cycles) (at 6 mA $cm^{-2}$, 1.24 – 1.87 V) |
| *Carbon* **2019**, *144*, 370 | Zn foil | | PVA gelled electrolyte | Bending (0, 90, 180°) | Disch. ~ 1.18 V Ch. ~ 1.90 V (at 2 mA $cm^{-2}$) | 1.35 V | - | 41.8 mW $cm^{-2}$ (at ~ 77 mA $cm^{-2}$) | > 25 hours (at 2 mA $cm^{-2}$, 1.18 – 1.9 V) |

* COF: Covalent organic framework, PVA: Poly(vinyl alcohol), RGO: Reduced graphene oxide

** Energy/power densities and cycle performance data were directly provided or calculated from the results of the previous studies.*