3D Porous Nb$_2$C MXene/Reduced Graphene Oxide Aerogel Coupled with NiFe Alloy Nanoparticles for Wearable Zn–Air Batteries

Hang Lei[1]‡, Shangjing Yang[2]‡, Runquan Lei[2], Qing Zhong[1], Qixiang Wan[1], Zhibin Li[2], Liang Ma[2], Shaozao Tan[1]*, Zilong Wang[2]*, Wenjie Mai[2]*

1. Guangdong Engineering & Technology Research Centre of Graphene-like Materials and Products, Department of Chemistry, College of Chemistry and Materials Science, Jinan University, Guangzhou 510632, P. R. China.

2. Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics, Jinan University, Guangzhou, Guangdong 510632, P. R. China.

‡ These two authors contributed equally to this work.

Corresponding Author

*E-mail addresses: zilong@email.jnu.edu.cn (Prof. Wang), tsztan@jnu.edu.cn (Prof. Tan), wenjiemai@email.jnu.edu.cn (Prof. Mai)

Key Words: Nb$_2$C MXene, Aerogel, Zn–Air Batteries, NiFe Alloy, Bifunctional Catalyst

1   Experimental Section
1.1 Preparation of Nb$_2$C MXene

The analytical balance was used to measure 1g of Nb$_2$AlC MAX powder (Forsman Scientific Co., Ltd), then 30 ml hydrofluoric acid was injected into a reactor. Afterwards, we carefully poured the Nb$_2$AlC powder into the reactor which filled with the hydrofluoric acid liquid. Then the reactor was transferred to the oil bath which has been heated to 60 °C, this etching reaction was kept for 48 hours under continuous stirring. After that, the resulting mixture was centrifuged at 4000 rpm and washed it with deionized water and absolute ethanol for 4 times. Finally, this product was freeze-dried.

1.2 Synthesize NiFe PBA

164.4mg of K$_3$[Fe(CN)$_6$] (99% AR) was dissolved in 48 ml of deionized water and sonicated for 30 minutes to get the solution A. After that, 244 mg Ni(Ac)$_2$·4H$_2$O and 356mg C$_6$H$_5$Na$_3$O$_7$·2H$_2$O were put into 32ml deionized water to from solution B. The solution A and B was mixed and magnetically stirred for five minutes. Later this product was static for 24 hours. Then we used a high-speed centrifuge with 10000 rpm to get the precipitate. Finally, it was dried at 60 °C for 24 hours to get the NiFe PBA.

1.3 Synthesis of NiFe/MG

100 mg of the prepared Nb$_2$C MXene was weighed, then added it into 40ml of deionized water. It was magnetically stirred for 2 minutes and then put it into ultrasonic cleaning machine for 15 minutes. Next a pipettor was used to measure the GO solution with a total content of 200 mg. The GO solution was added to the MXene solution under stirring, and continue sonicating for 30 minutes. Afterwards, 150 mg NiFe PBA and 200mg C$_6$H$_8$O$_6$ were added into the system. Then the system under hydrothermal

conditions at 95 °C for 5 hours. What follows is centrifuging it with the condition of 4000 rpm, then it washed with absolute ethanol and deionized water twice. A solution of ethanol and water was prepared at a ratio of 1:9, then we mixed it well with the centrifuge product and frozen it in the refrigerator. After that, it was freeze-dried for 48 hours to get the aerogel end product. The aerogel was heated at 600 °C for 2 hours in the Ar atmosphere to get NiFe/MG.

1.4 Characterization

Based on a Cu Kα radiation source (λ = 1.540 56 Å), the X-ray diffraction (XRD, Bruker D8 advance) was operated at 40 kV and 40 mA. It's a useful way to analyze the morphology and structure by field-emission scanning electron microscopy (FE-SEM, ZEISS ULTRA 55) and transmission electron microscope (TEM, JEOL JEM 2100F). The surface chemical compositions of the samples were performed by X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific). Under the condition that the laser wavelength is 532 nm, Raman spectra were recorded with Lab RAM HR Evolution. An inductively coupled plasma-mass spectrometry (ICP-MS) was carried out using Agilent ICPMS 7700. The N_2 adsorption–desorption was measured with ASAP 2460 Version 2.01 (Micrometrics).

1.5 Electrochemical test

For oxygen evolution reaction (OER), the catalyst ink prepared process of the working electrode is as follows: 5 mg NiFe/MG and 1mg carbon black were weight and added into a mixed liquid system which was formed by 980 μL absolute ethanol and 20μL Nafion solution (5.0 wt%). Then it was sonicated for 30 minutes to obtain an average suspension. The working electrode was made up of 100 μL catalyst inks

dripped onto a carbon cloth (1 cm^{-2}). A graphite rod and a Hg/HgO electrode were separately as the counter and reference electrodes, respectively. Electrochemical workstation (CHI 660E) was used to furnish the working electrode with potentials. All the measurements were operated at room temperature. The scan rate was 5 mV/s^{-1} for Linear sweep voltammetry (LSV) test. The electrochemical active surface area (ECSA) of the catalysts based on their double-layer capacitances (C_{dl}), the ECSA is generally proportional to the C_{dl} of the electrocatalysts. Specifically, scan-rate dependence of cyclic voltammograms (CVs) is performed in the potential range of 0.9254–1.025 V without redox processes to obtain the capacitive current associated with double-layer charging for NiFe and NiFe/MG. Then the C_{dl} can be obtained by plotting the $\Delta j = (j_a - j_c)/2$ at 0.9754 V versus reversible hydrogen electrode (RHE) against the scan rate. Considering oxygen reduction reaction (ORR) measurement, 5μL catalyst inks was dipped onto a rotating disk electrode (RDE) with diameter of 5.0 mm. The RDE, counter and reference electrodes were put into the O$_2$-saturated 0.1M KOH solution, while different rotating rate (i.e., 625, 900, 1225, 1600, 2000 and 2500 rpm) were chosen for LSV measurement. The Koutecky–Levich (K–L) plots were evaluated at various potentials, the number of electrons transferred (n) is calculated from the following equations:

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

$$B=0.62nFC_O(D_O)^{2/3}\upsilon^{-1/6}$$

$$J_K = nFkC_O$$

where the parameters explain as follows: kinetic current density (J_K), measured

current density (J), diffusion limited current density (J_L), rate of electrode rotation (ω) in rpm, Levich slope (B), Faraday constant (F = 96485 C mol^{-1}), bulk concentration of O_2 (Co = 1.2 × 10^{-3} mol L^{-1}), kinematic viscosity of the electrolyte (υ= 1.09 × 10^{-2} cm^2 s^{-1}), diffusion co-efficient of O_2 (D_O = 1.90 × 10^{-5} cm^2 s^{-1}), electron transfer rate constant (k) and number of electronic transferred (n).

1.6 Electrochemical test of the liquid Zn-air battery

A home-made liquid Zn-air battery was chosen to measure the electrochemical performance. The manufacture process of air cathode is as followed: the catalyst ink as same as above electrochemical measurement, 200 μL catalyst ink was drop onto the nickel foam of 1 cm^{-2}. Next, gas diffusion layer (GDL) and separator (pp2332) were put at the opposite side of the nickel foam. GDL was located on the air-facing side while separator (pp2332) was situated on the solutional side. The well-polished zinc sheet (99.9 % metal basis, thickness is 0.1 mm) was chosen as for the anode material. Besides, a solution composed of 6 M KOH and 0.2 M Zn(Ac)$_2$ was used as the electrolyte. The assembled Zn-air batteries were put at room condition without additional oxygen feed to do all measurements. The power density and open circuit voltage were measured through the methods of Linear Sweep Voltammetry (LSV) and Open Circuit Potential (OCP), respectively. The specific capacity, energy density and energy efficiency were calculated according to the equation as follows:

$$Specific\ capacity = \frac{current \times service\ hours}{weight\ of\ consumed\ zinc}$$

$$Energy\ efficiency = \frac{E_{discharge}}{E_{charge}} \times 100\% = \frac{U_{discharge}}{U_{charge}} \times 100\%$$

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

1.7 Electrochemical test of the flexible battery

400 μL aerogel catalyst ink was evenly dropped onto the nickel foam of 4 cm^{-2}. In order to get the gel polymer electrolyte, 5.0 g polyvinyl alcohol (PVA) powder (MW 88000, ACROS) was poured into 50.0 mL deionized water and stirred 2 hours at 95°C, then 5.05 g KOH with 0.092 g Zn(Ac)$_2$ acetate was added to the solution and stirred at 95°C for 40 minutes. Later the colloidal fluid was placed into the petri dish. Moreover, transferred the petri dish to the fridge for 12 h. Inked nickel foam, gel polymer electrolyte and polished Zn sheet (99.9 % metal basis, thickness is 0.1 mm) were stacked into a three-layer structure to make up of the flexible battery. The test method is similar to that of liquid ZAB.

2. Supplementary Figures
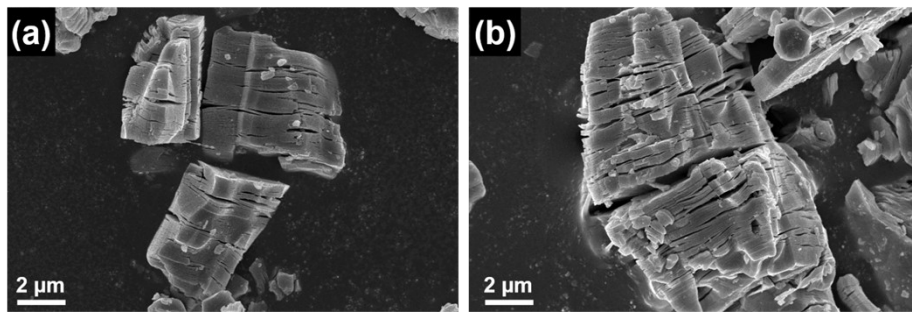
Figure S1. SEM patterns of (a, b) Nb_2C MXene.
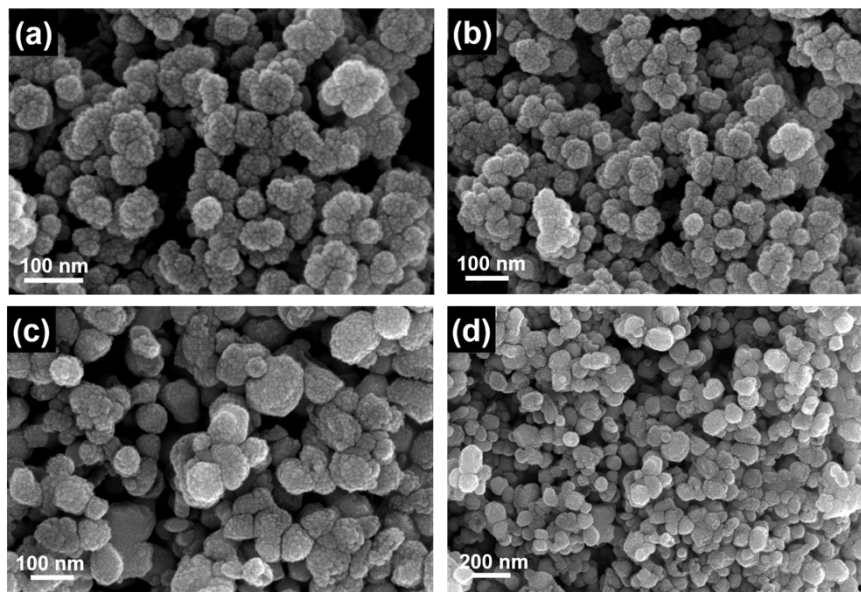
Figure S2. SEM patterns of (a, b) NiFe PBA and (c, d) NiFe alloy.
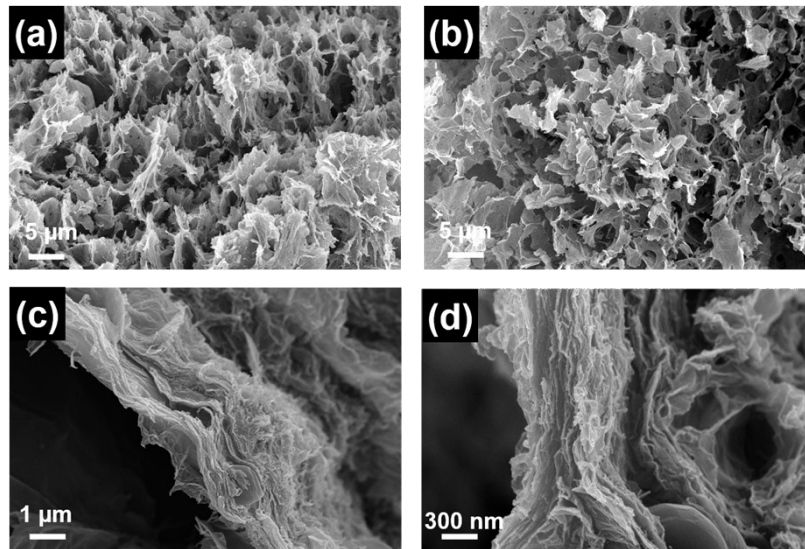
Figure S3. SEM patterns of (a) MG and (b, c, d) NiFe/MG at different magnifications.
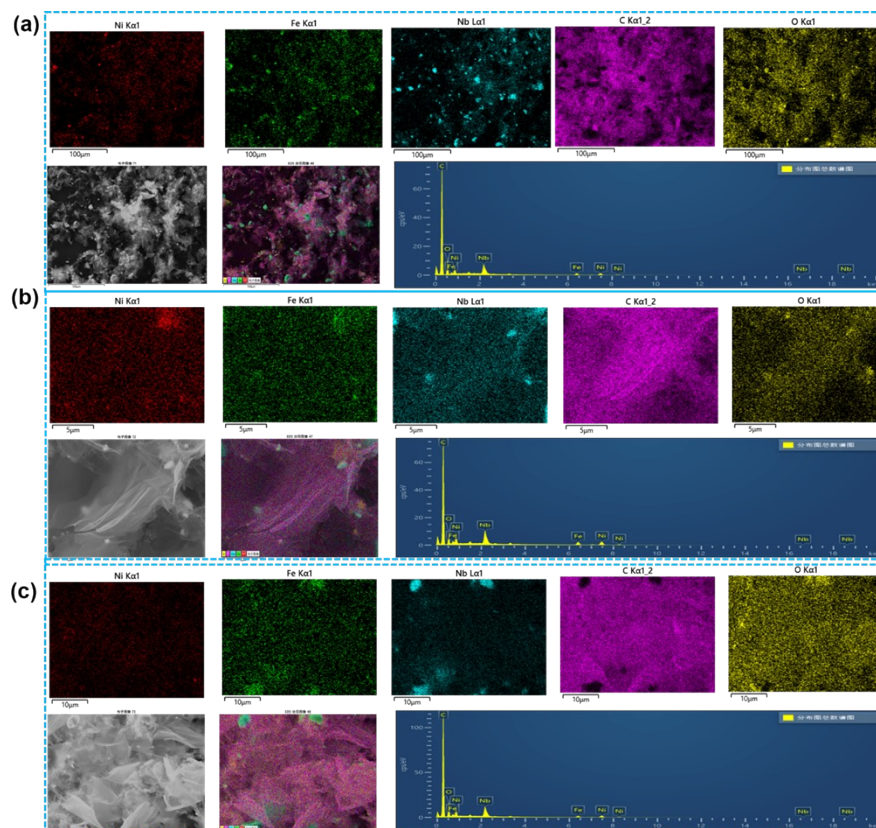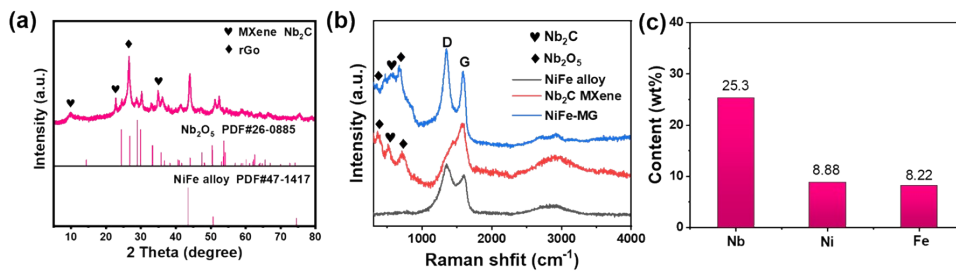

Figure S4. (a-c) SEM image of NiFe/MG and corresponding element mapping images
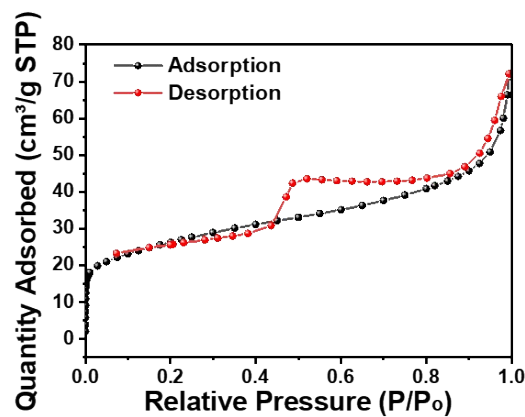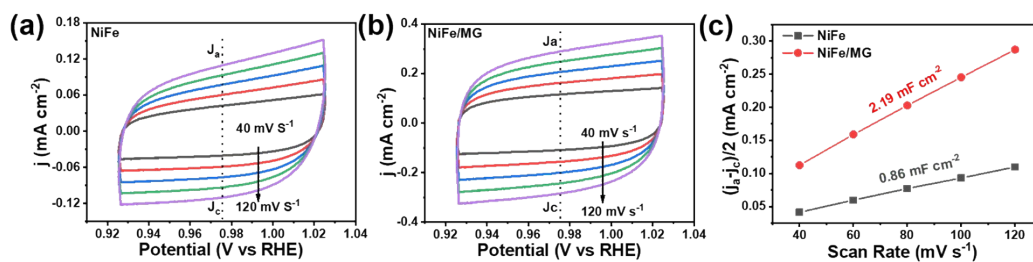
in different parts.
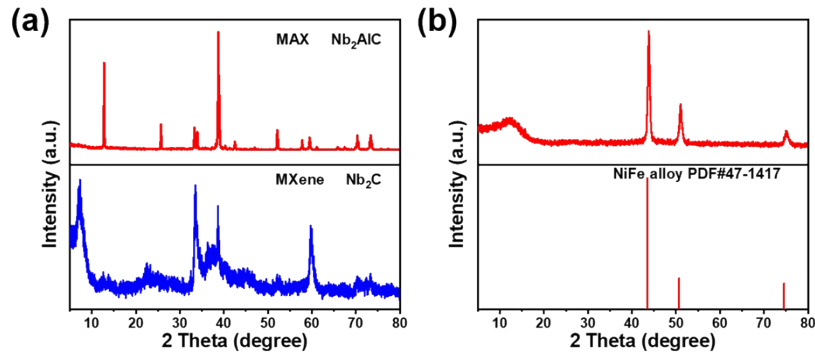
Figure S5. (a) XRD patterns of Nb$_2$AlC MAX and Nb$_2$C MXene. (b) XRD pattern of NiFe alloy.

Figure S6. (a) XRD patterns of NiFe/MG. (b) Raman spectra of NiFe alloy, Nb$_2$C MXene and NiFe/MG. (c) The content of Nb, Ni and Fe was measured by inductively coupled plasma-mass spectrometry.
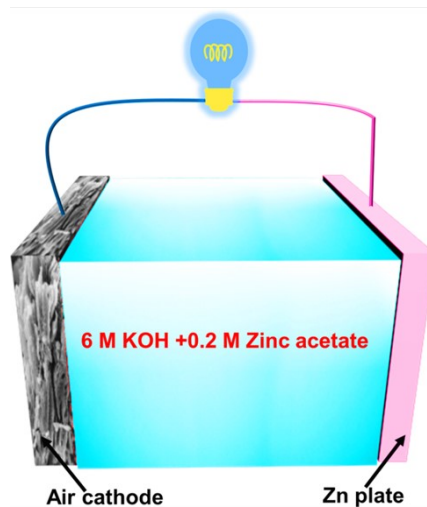

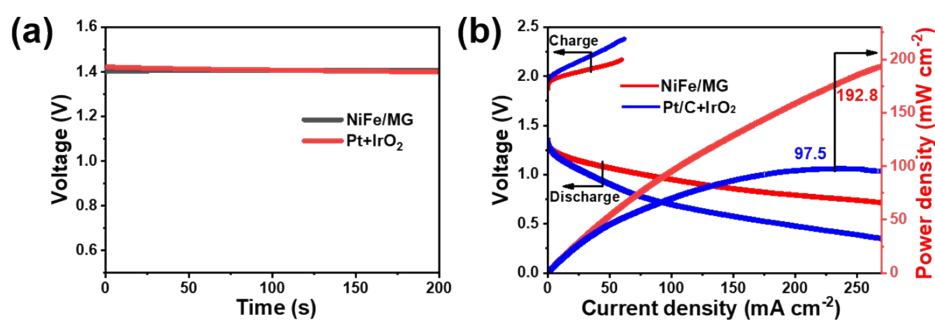**Figure S7.** Nitrogen adsorption-desorption isotherms of NiFe/MG.

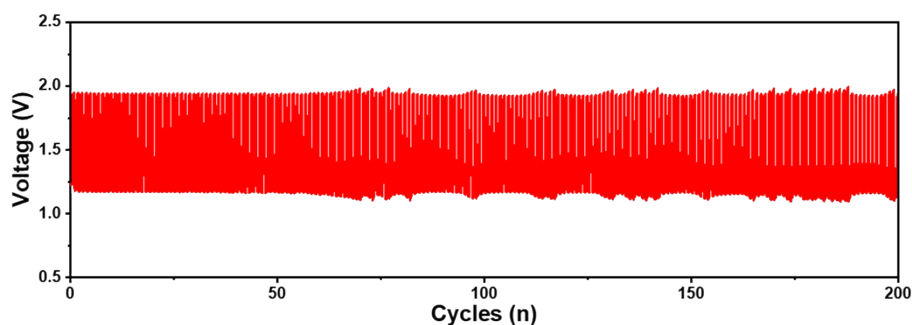**Figure S8.** Cyclic voltammetry of a) NiFe and b) NiFe/MG at different scan rate. c) Electrochemical surface areas of NiFe and NiFe/MG.
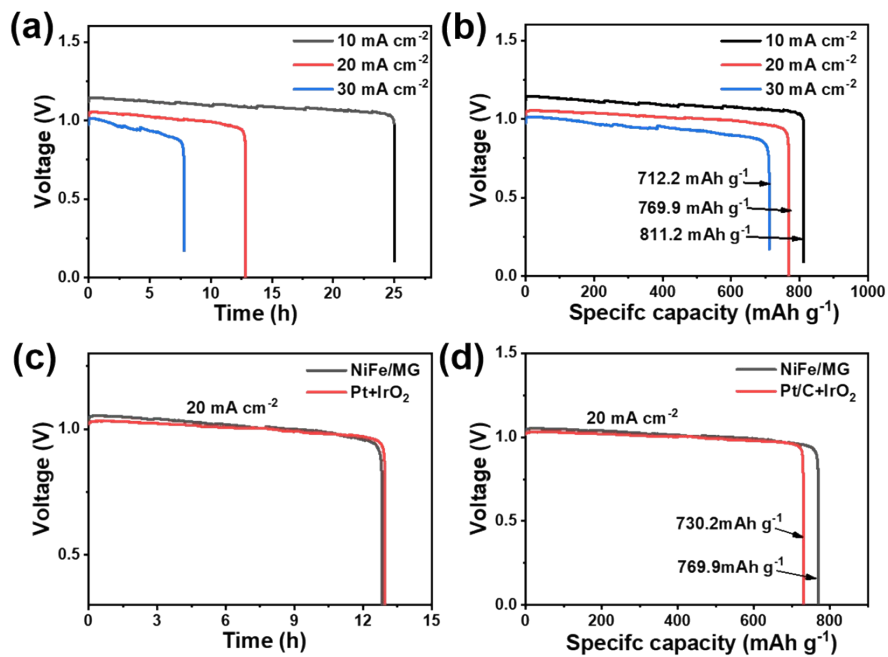

**Figure S9.** Schematic diagram of homemade liquid zinc-air battery.

Figure S10. (a) Open circuit voltages and (b)Power density curves of zinc-air batteries based on NiFe/MG and Pt+IrO$_2$ catalysts.

Figure S11. Cyclic stability of NiFe/MG liquid Zn air battery at a current density of 2 mA cm^{-2}.

Figure S12. (a, b) The galvanostatic discharge curves and corresponding specific capacity curves of the NiFe/MG ZAB at various current densities. (c, d) The galvanostatic discharge curves and corresponding specific capacity curves of NiFe/MG and Pt/C + IrO$_2$ ZABs at a discharge current density of 20 mA cm^{-2}.
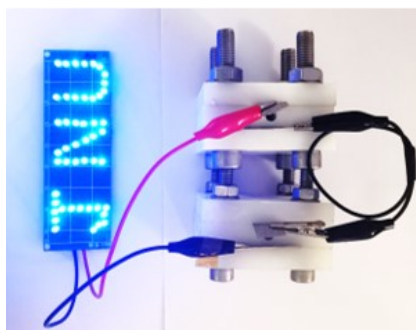
Figure S13. Display diagram of liquid Zn-air batteries powered light emitting diode light board.