Magnetohydrodynamic effect enables dendrite-free Zn anode in alkaline electrolytes

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Experimental Section

Magnetic Field Setup: A permanent magnetic field generator (PS-YCT150-12, Hunan Paisheng Technology Co, Ltd) was customized to obtain a horizontal magnetic field. A uniform magnetic field was generated between the N pole and S pole. The intensity of the magnetic field was controlled by adjusting the distance between two magnetic poles and was measured by a high precision gauss meter (TD 8620, Changsha Tunkia Co, Ltd).

Electrochemical Testing and Characterization: The composition of the electrolyte was 6 M KOH with 0.2 M ZnO. During the electrochemical test, an external magnetic field with the intensity of 0.4 T parallel to the current direction was obtained by sandwiching the battery between the N pole and S pole. The chronoamperometric and EIS tests were carried out in a three-electrode system with a reference electrode of Hg/HgO, a counter electrode of platinum, and a working electrode of Zn.

The Electrodeposition of Zn: The in-situ observation of the electrodeposition behavior of Zn on the Cu current collector was carried out in a transparent cuboid electrolytic cell (1 cm in length, 1 cm in width, and 4 cm in height) recording by an industrial microscope (KY-H3800S42, KangYuan Electronic). The microstructures of the Zn deposits were characterized by scanning electron microscope (SEM, TESCAN, Vega3 SBH). The surface roughness was measured by the confocal laser scanning microscope (CLSM, KEYENCE VK-X1100). The element mapping was analyzed by energy dispersive spectrometer (EDS, Bruker Nano Gmbh, XFlash Detector 630M). The crystal structure and diffraction peak intensity were obtained by X-ray diffraction (XRD, Rigaku MiniFlex600).

Symmetric Battery Test: Small cuboid cuvettes were used to assemble symmetric batteries. Both the anode and cathode were Zn plates, and the gap between the two electrodes was 2 mm. The commercial non-woven fabric was used as the battery separator. The long galvanostatic cycling was tested by the LAND system at 25 °C.

Zn-Air Battery Test: To prepare the air cathode, 5 mg Pt/C and 5 mg RuO_2 were dispersed in 1 mL mixed solution containing 475 μL 2-propanol, 475 μL deionized water, 50 μL 5 wt.% Nafion solution (19:19:2) and ultrasonic treatment. Then the homogenous suspensions were dripped on hydrophobic carbon cloth and dried at 60 ℃ with the loading mass of 1 mg cm^{-2}. The Zn plate served as the anode, the commercial non-woven fabric served as the separator, and a homemade device was used for the Zn-Air battery test. Galvanostatic cycling test was conducted by the LAND system at a current density of 10 mA cm^{-2} with 10 min discharge/charge.

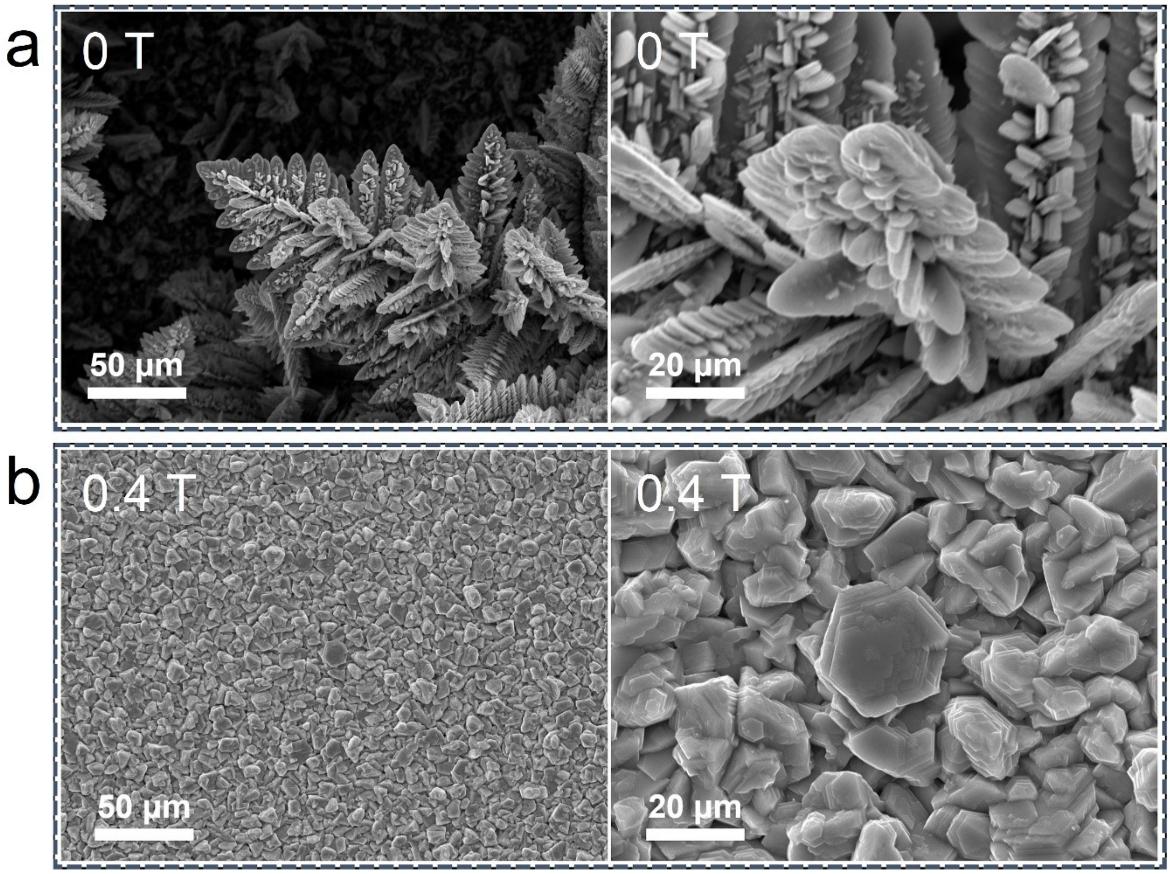

Figure S1. SEM images of Zn deposits. a) Without the magnetic field. b) With the magnetic field.

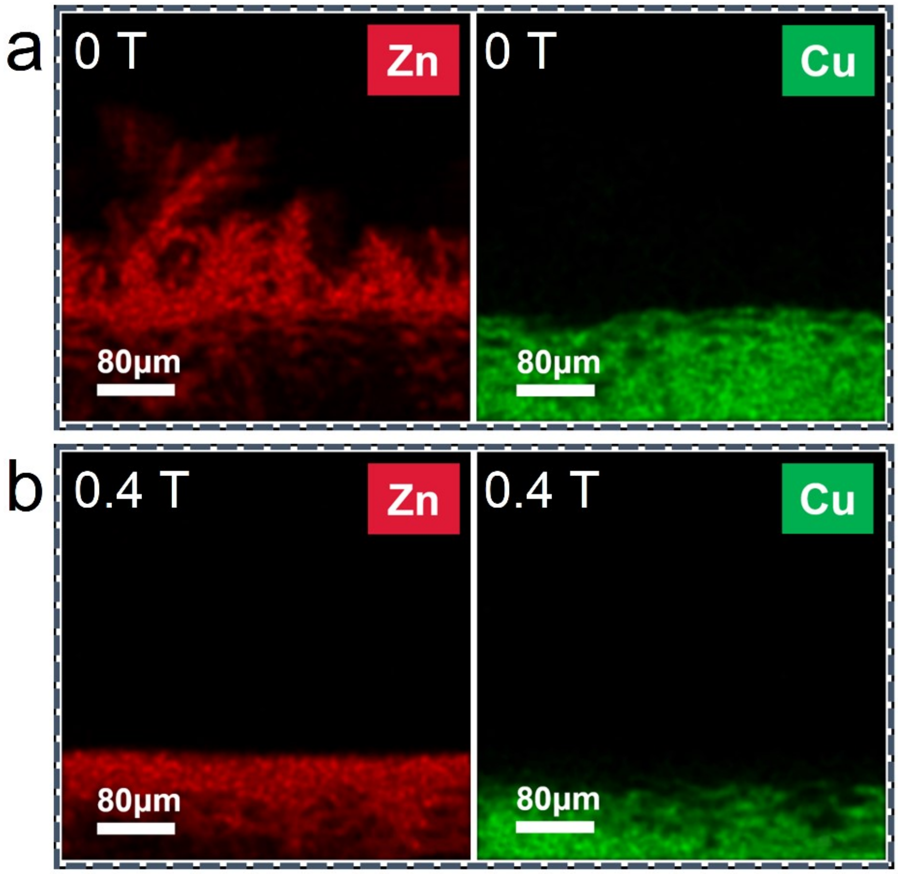

Figure S2. The mapping of Zn deposits obtained a) without or b)with the magnetic field.

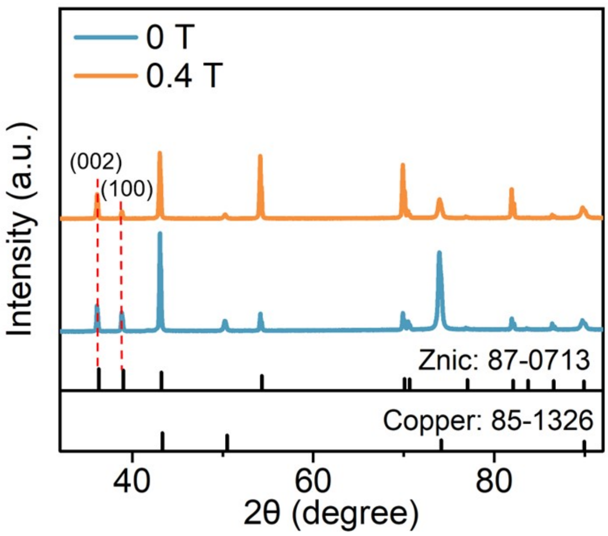

Figure S3. The XRD of Zn deposits obtained without/with the magnetic field.

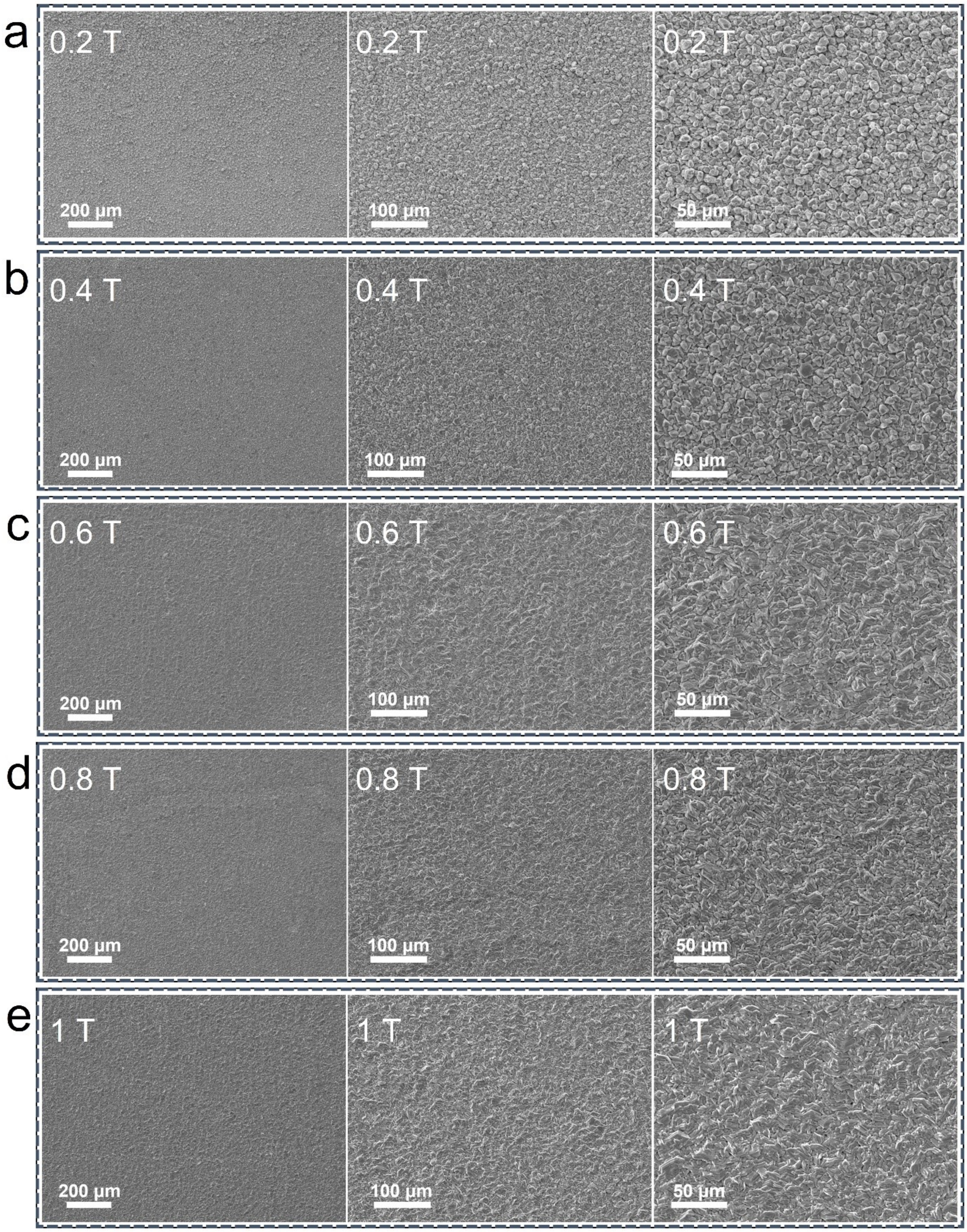

Figure S4. SEM images of Zn deposits with the magnetic field strengths of a) 0.2 T, b) 0.4 T, c) 0.6 T, d) 0.8 T and e) 1 T.

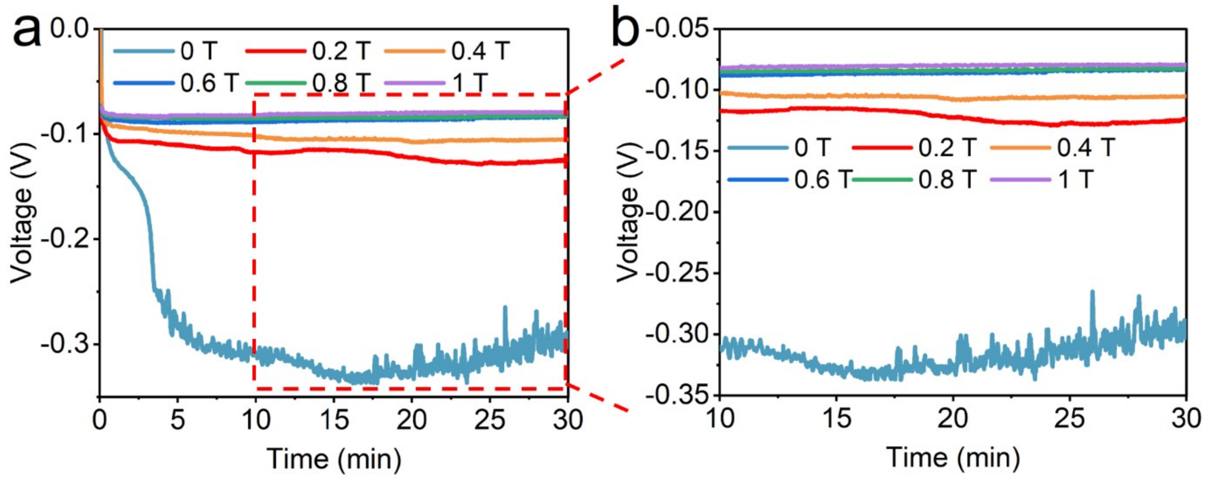

Figure S5. a) The overpotential of Zn electrodeposition with different magnetic field strengths. b) The amplified voltage curve in the red dashed box.

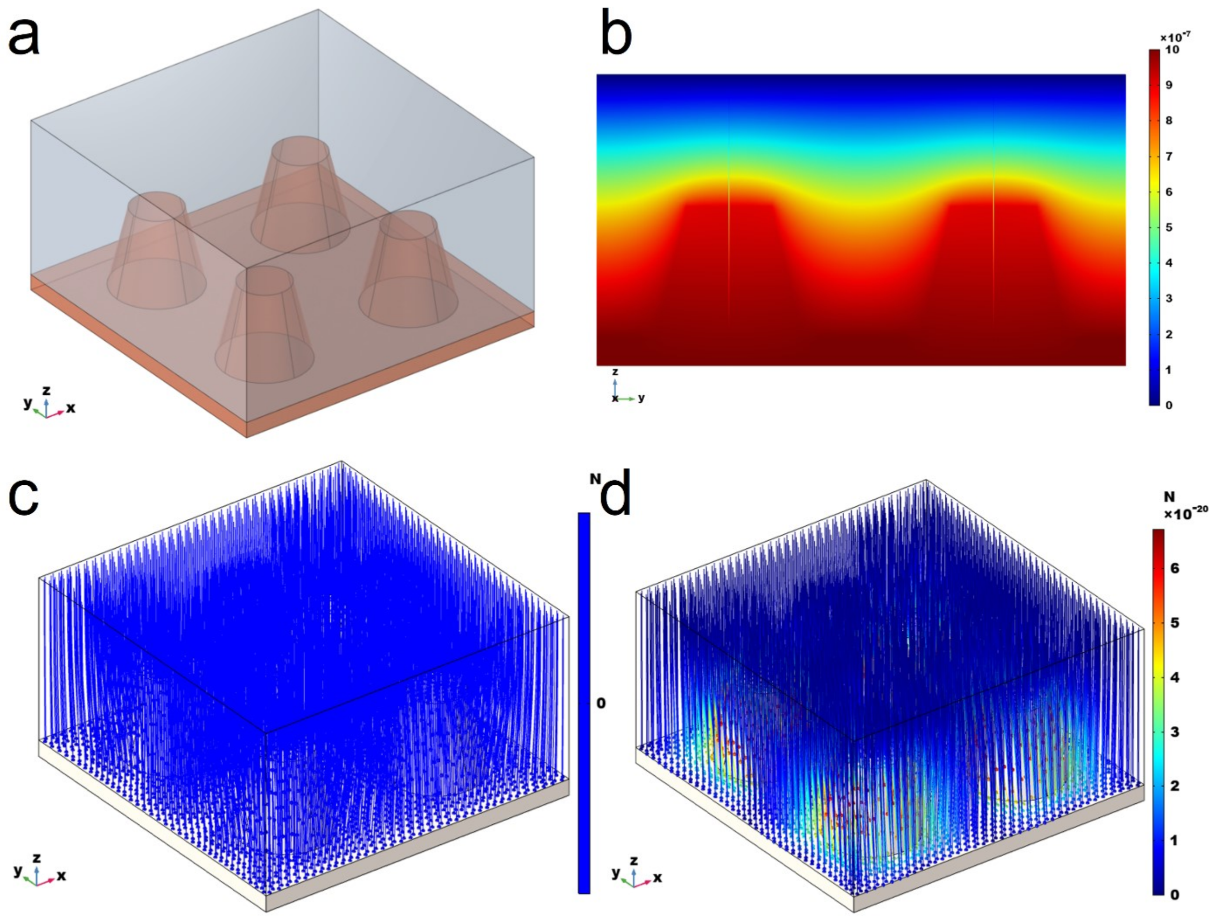

Figure S6. a) Framework models for simulation. b) Simulated electric field distribution. Simulation results of the distribution of Lorentz force c) without or d) with the magnetic field.

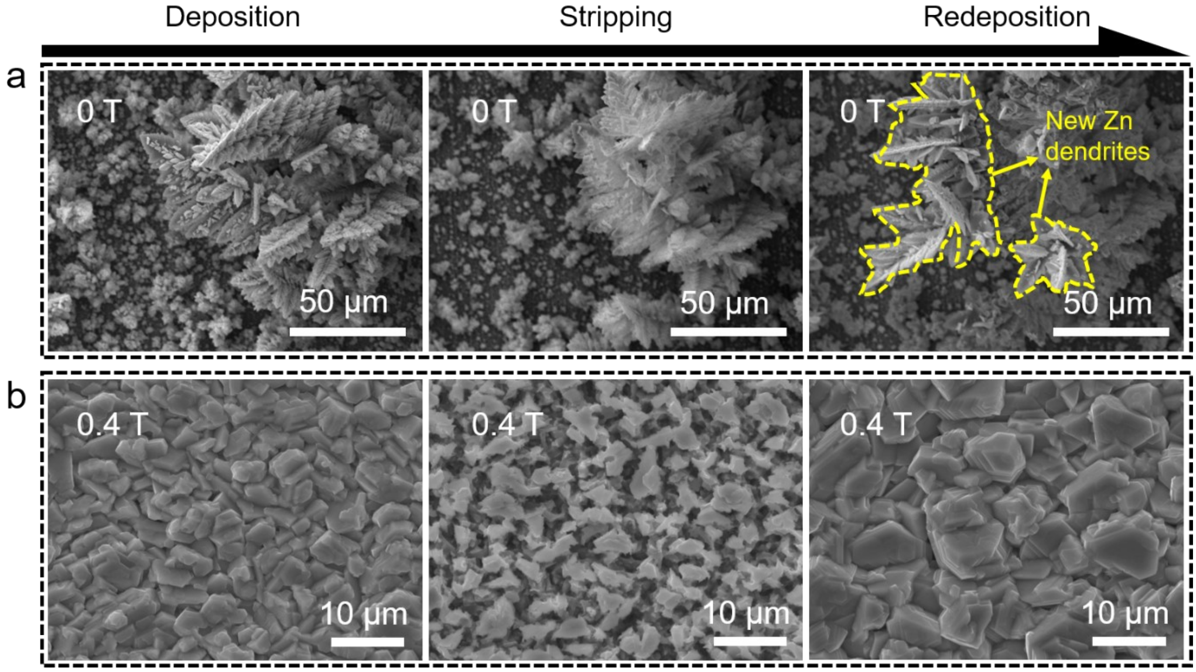

Figure S7. The semi in-situ SEM characterization of Zn deposition/stripping morphology a) without or b) with the magnetic field.

To further demonstrate the suppressive effect of the magnetic field on Zn dendrite, the semi in-situ SEM characterization during Zn deposition/stripping cycle was carried out. In the experiment, Zn electrodeposition was first performed for 10 min, followed by stripping for 5 min and finally redeposit for 10 min. The surface of the electrode at the same location after the cycle was characterized by SEM. As shown in Fig. S7, the SEM morphologies of the Zn surface after deposition/stripping/redeposition are shown in the three columns of images from left to right, respectively. As shown in Fig. S7a, sharp Zn dendrites appeared when electrodepositing for 10 min without the magnetic field. After stripping 5 min, the Zn dendrites were not completely dissolved and the sharp structure still existed. After redepositing for 10 min, the previous Zn dendrites further expanded, and the larger and sharper dendrite growth happened. In contrast, after the magnetic field was applied, as shown in Fig. S7b, the Zn deposit was flat and compact with no dendrite during the whole cycle. The result indicates that the magnetic field can effectively promote the uniform Zn deposition during the deposition/stripping cycle.

The Zn deposition/stripping equations in alkaline solution are illustrated below:

Discharging process:

Oxidation:

$$Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^- \quad (1)$$

ZnO precipitation:

$$Zn(OH)_4^{2-}(aq) \rightarrow ZnO(s) + H_2O(aq) + 2OH^-(aq) \quad (2)$$

Charging process:

$$ZnO(s) + H_2O(aq) + 2OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) \quad (3)$$

$$Zn(OH)_4^{2-}(aq) + 2e^- \rightarrow Zn(s) + 4OH^-(aq) \quad (4)$$

Overall reaction:

$$Zn(s) + 2OH^-(aq) \leftrightarrow ZnO(s) + H_2O(aq) + 2e^- \quad (5)$$

The chemical reaction equations of the Zn-Air battery are listed below:

Anode:

$$Zn(s) + 4OH^-(aq) \leftrightarrow Zn(OH)_4^{2-}(aq) + 2e^- \quad (1)$$

$$Zn(OH)_4^{2-}(aq) \leftrightarrow ZnO(s) + H_2O(aq) + 2OH^-(aq) \quad (2)$$

Cathode:

$$O_2 + 2H_2O(aq) + 4e^- \leftrightarrow 4OH^-(aq) \quad (3)$$

Overall reaction:

$$2Zn(s) + O_2 \leftrightarrow 2ZnO(s) \quad (4)$$

Video S1. The in-situ observation of the Zn electrodeposition process without the magnetic field.

Video S2. The in-situ observation of the Zn electrodeposition process with the magnetic field.