Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

for

Ultrafine $CoFe_2O_4$ quantum dots as oxygen electrocatalyst for rechargeable zinc air batteries

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Experimental section

Chemicals: Cobalt acetate tetrahydrate ($Co(Ac)_2 \cdot 4H_2O$), benzylamine (>98%) and ammonia solution were obtained from Aladdin Co. Ltd. Commercial Pt/C (20%) and iridium dioxides (IrO_2) were purchased from Alfa Aesar. Poly(vinyl alcohol) (PVA) and potassium hydroxide (KOH) were supplied by Sinopharm Chemical Reagent Co. Ltd.

Synthesis of electrocatalyst: 80 mg of $Co(Ac)_2 \cdot 4H_2O$ was dispersed into 3.5 mL of benzylamine in a three-neck flask; the solution was vigorously stirred for 120 min. 4.5 mL of KOH was slowly added to the resultant and refluxed at 165 ^oC for 300 min. Then, after cooling to 25 ^oC, the solution was centrifuged at 10000 rpm for 10 min and washed with ethanol for several times to collect the solid products. The powder was secondarily washed with 0.5 M H_2SO_4 and deionized water to obtain Co_3O_4 QDs. The synthetic method was similar for $CoFe_2O_4$ QDs except with the presence of ferric acetate.

Characterization: X-Ray Powder Diffraction (XRD) was carried out with Bruker D8 diffractometer. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were recorded on a JEOL-2010F with a field emission gun operating at 200 kV to analyze the morphology of the as-prepared catalyst. X-ray photoelectron spectroscopy (XPS) was measured with Kratos Axis Ultra DLD analyzer operating at pass energy of 30 eV. The carbon 1s peak of the pollutant carbon was calibrated at 284.8 eV.

Electrochemical measurements: A three-electrode system was used to test the activities of as-prepared catalyst in O_2-saturated 1M KOH electrolyte at room temperature. A Hg/HgO (saturated 1M KOH) electrode was used as the reference electrode and carbon rod as the counter electrode. For ORR measurement, the catalyst was loaded onto the platinum-carbon electrode (4 mm diameter) as a working electrode for testing at a scan rate of 10 mV s^{-1}. To prepare the catalyst ink, 1 mg of catalyst was dissolved in 600 mL of deionized water, 380 mL of isopropanol, 20 mL of Nafion solution. After 30 min of sonication, the homogeneous catalyst solution was dropped onto the RDE (loading: 0.285 mg cm^{-2}). The ORR polarization curves were collected at various rotation rates (400, 600, 800, 1200, 1600 and 2400 rpm) for calculating the transferring electron number by K-L equation. For OER measurement, the 2 mg catalyst was sprayed onto 1×1 carbon paper as a working electrode for testing. The catalyst loading on carbon paper was controlled to 2 mg cm^{-2}. The carbon paper without microporous layer (MPL) was utilized to alleviate the gas transfer resistance during test. The polarization curve was obtained with a sweep speed of 5 mV s^{-1} in the range of 1.2 V to 1.7 V vs. RHE. Electrochemical impedance spectroscopy (EIS) analysis was tested in the frequency range of 100 kHz to 0.01 Hz.

Aqueous Zn-Air Batteries: All electrochemical tests are performed under ambient air. 6 M KOH (with 0.2 M ZnAc) solution was used as electrolyte to ensure reversible Zn electrochemical reactions. Zinc plate (0.5×3 cm^2), catalyst-loaded carbon paper (1 cm^2) as anode and gas diffusion layer, respectively. 2 mg catalyst was dispersed in 1mL ethanol and 20 uL of Nafion solution. The catalyst was sprayed onto a carbon

paper for testing. For Pt/C-IrO_2 electrocatalyst, the catalyst loading was 0.285 mg cm^{-2}.

All-solid-state Zn-Air battery: Polymer electrolytes were synthesized according to previously reported methods. Briefly, PVA membrane was doped with 8 M KOH electrolyte for 12 h to adsorb KOH for efficient ionic conductivity. The doping level was calculated to 380%. Assembly of PVA film in the middle of a zinc plate and catalyst-loaded carbon paper (loading: 2 mg cm^{-2}) to form an all-solid zinc-air battery.

Table S1 XPS analysis of Co_3O_4-QDs, $CoFe_2O_4$-QDs and $CoFe_2O_4$-QDs after 3000 cycles.

Electrocatalyst	Co^{2+}/Co^{3+} ratio	Oxygen defect
Co_3O_4-QDs	1.3	28%
$CoFe_2O_4$-QDs	1.5	41%
$CoFe_2O_4$-QDs after 3000 cycles	1.4	36%

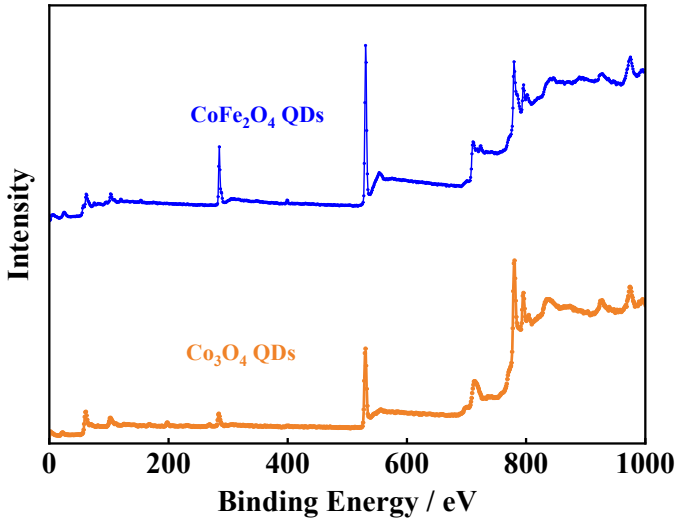

Figure S1 XPS survey scan of Co_3O_4 QDs and $CoFe_2O_4$ QDs electrocatalysts.

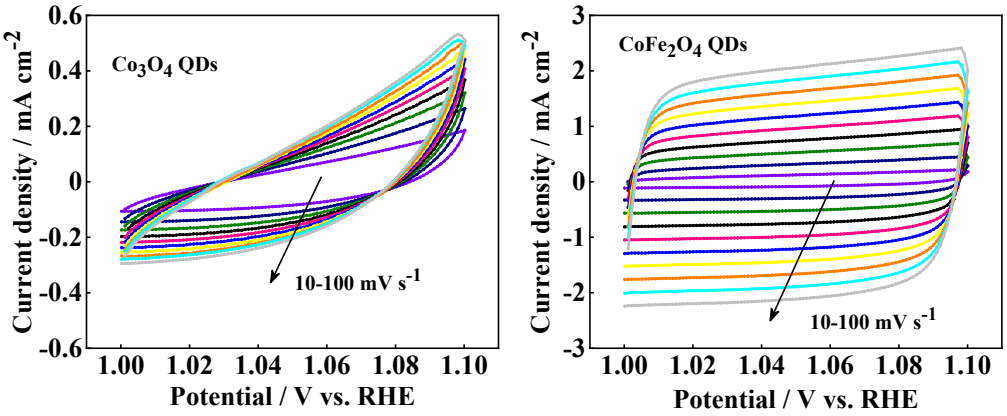

Figure S2 Cyclic voltammetry curves of Co_3O_4 QDs and $CoFe_2O_4$ QDs electrocatalysts.

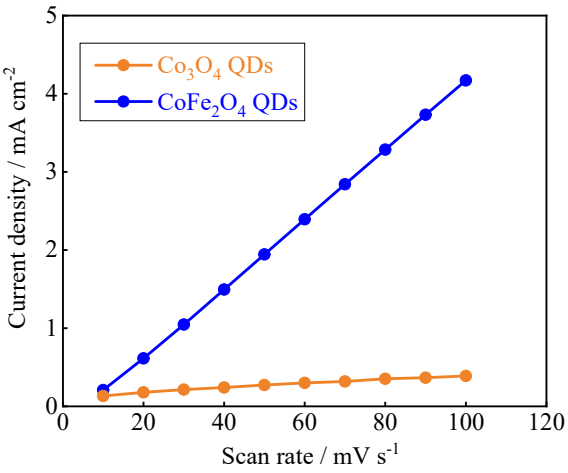

Figure S3 Double layer capacitance of Co_3O_4 QDs and $CoFe_2O_4$ QDs electrocatalysts.

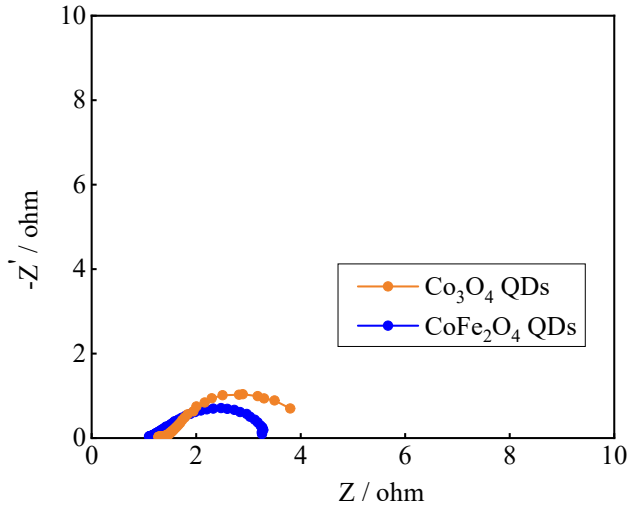

Figure S4 Electrochemical impedance spectroscopies of Co_3O_4 QDs and $CoFe_2O_4$ QDs electrocatalysts.

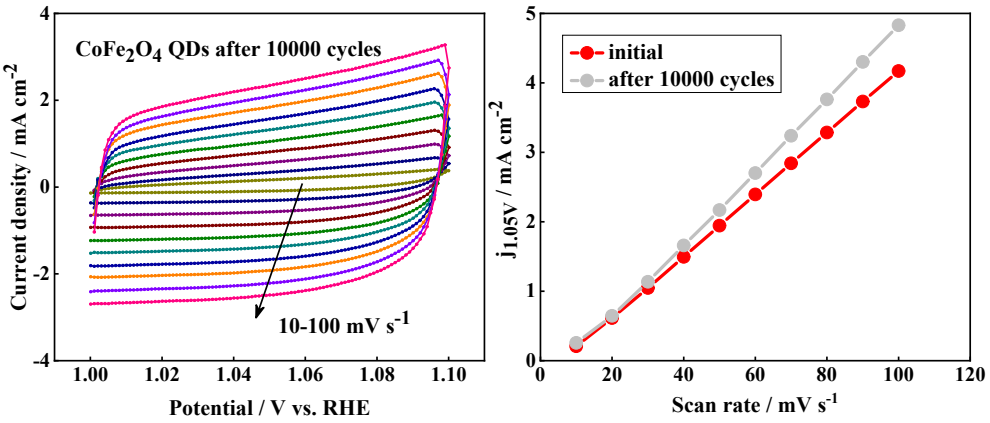

Figure S5 Cyclic voltammetry curves and double layer capacitances of $CoFe_2O_4$ QDs after 10000 cycles.

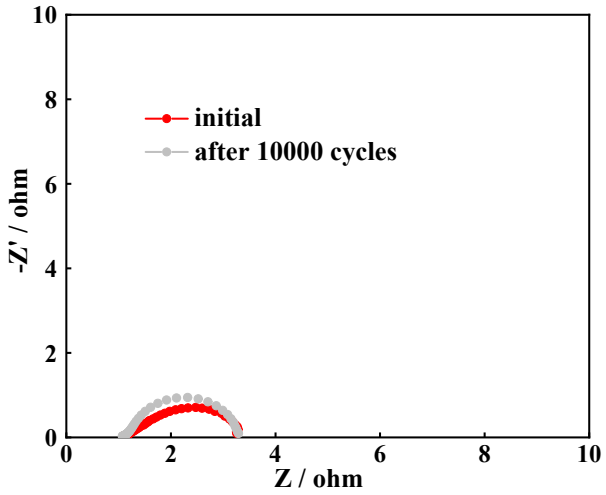

Figure S6 Electrochemical impedance spectroscopies of $CoFe_2O_4$ QDs before and after 10000 cycles.

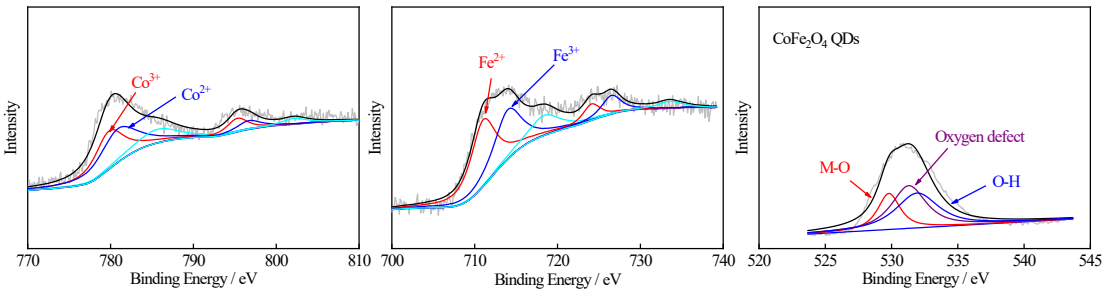

Figure S7 XPS of $CoFe_2O_4$-QDs after 3000 cycles.

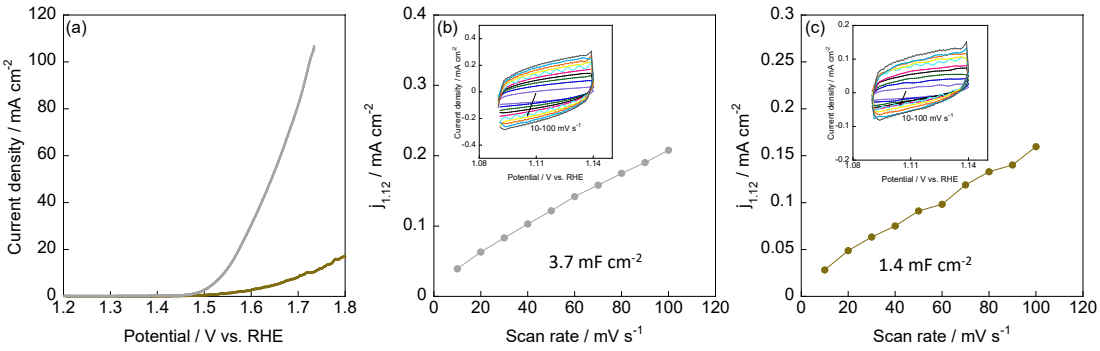

Figure S8 LSV curves and double layer capacitance of commercial IrO_2 before and after stability test.

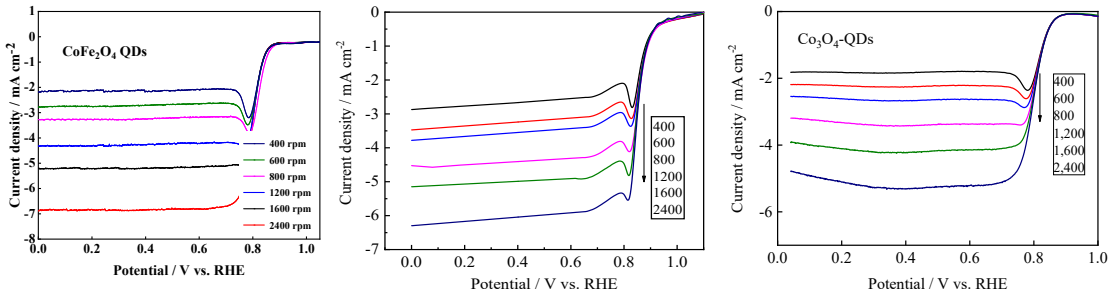

Figure S9 LSV curves of Pt/C, Co_3O_4 QDs and $CoFe_2O_4$ QDs electrocatalysts.

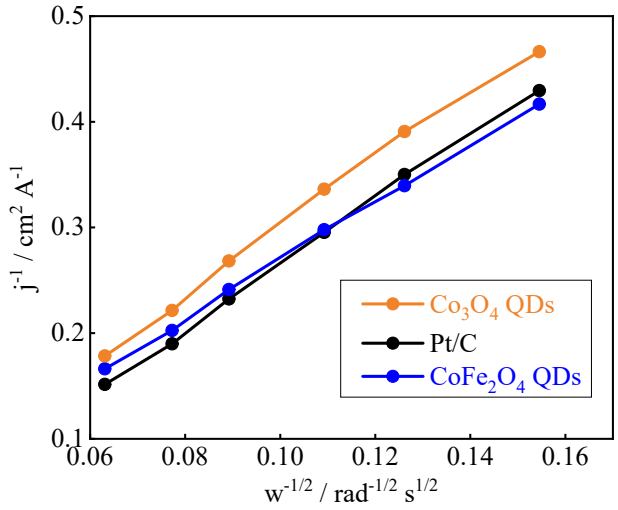

Figure S10 Koutecky-Levich curves of Co_3O_4 QDs, Pt/C and $CoFe_2O_4$ QDs.

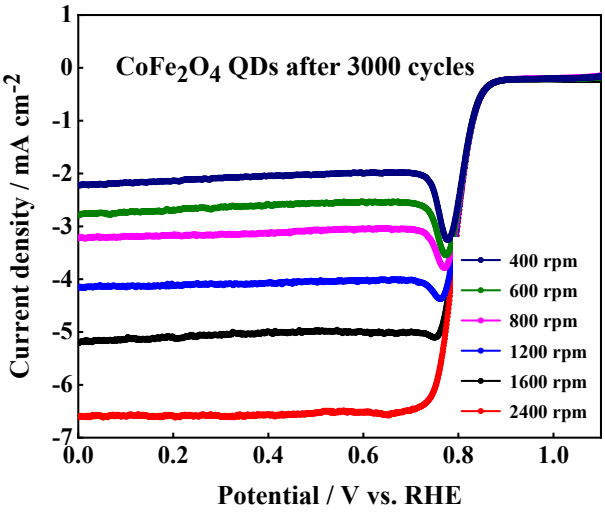

Figure S11 LSV curves of $CoFe_2O_4$ QDs electrocatalysts after 3000 cycles.

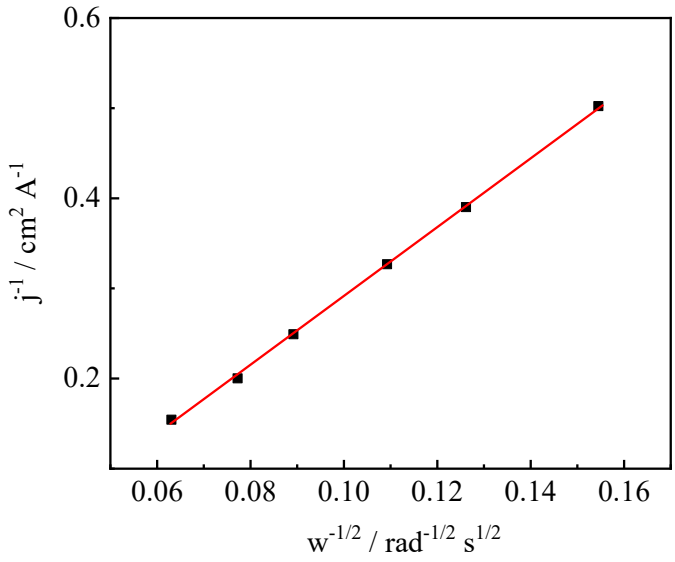

Figure S12 Koutecky-Levich curves of $CoFe_2O_4$ QDs after 3000 cycles.

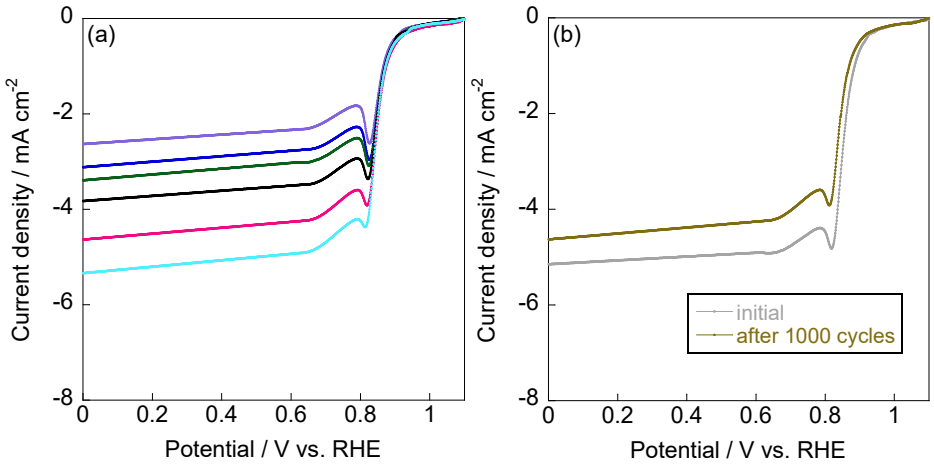

Figure S13 Stability test of commercial Pt/C before and after 1000 potential cycles.

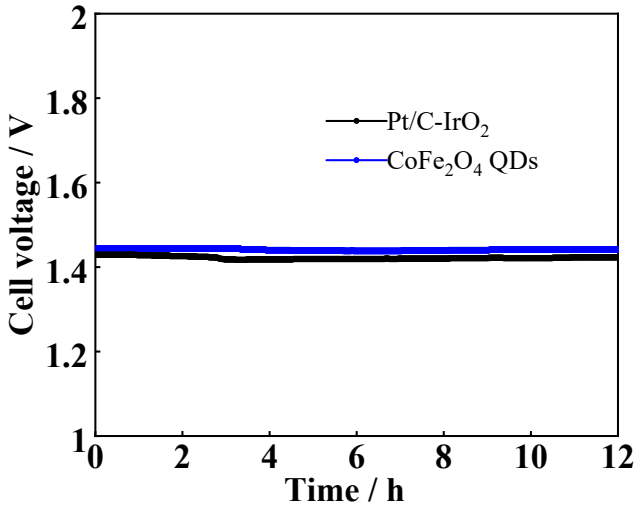

Figure S14 Open circuit voltage tests of Pt/C-IrO_2 and $CoFe_2O_4$ QDs.

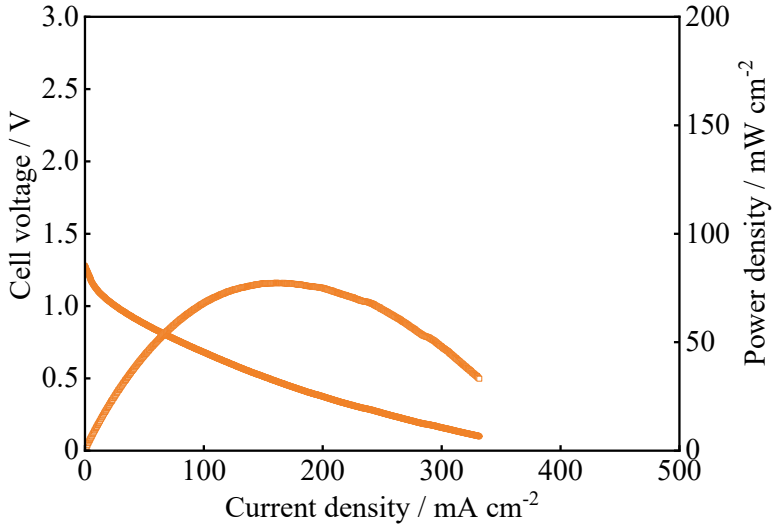

Figure S15 I-V polarization and power density curves of Co_3O_4 QDs based rechargeable zinc air battery.

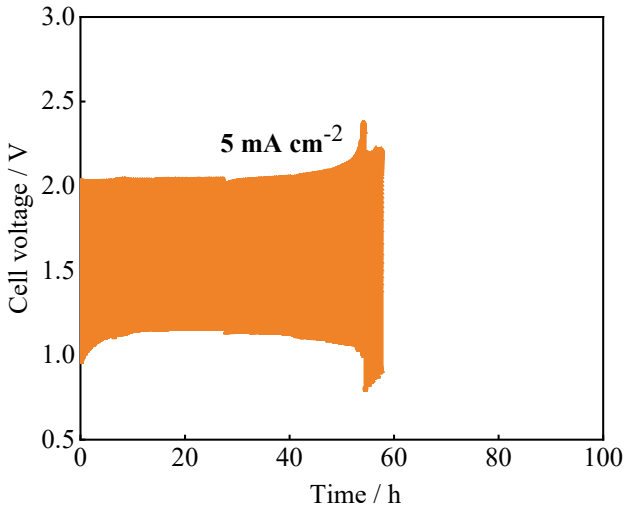

Figure S16 Stability test of Co_3O_4 QDs based rechargeable zinc air battery.