Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

for

Electronically interacted Co_3O_4/WS_2 as superior oxygen electrode for rechargeable zinc-air batteries

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Experimental section

Synthesis of WS_2: 1 g of $(NH_4)_6H_2W_{12}O_{40}\cdot XH_2O$ and 17 mL of $(NH_4)_2S$ solution were heated at 70 ^oC and 2 M HCl was added to the above mixed solution. The resultant precipitate was washed to neutral and dried in oven at 50 ^oC. The powder was placed in a tubular furnace and kept calcination at 450 ^oC for 4 h in an Ar/H_2 atmosphere with the heating up of 5 ^oC min^{-1}. The obtained black powder was placed in the 2 M KOH solution for ultrasonic cleaning, then washed with water to neutral and the pure phase WS_2 was obtained after drying at 50 ^oC.

Synthesis of Co_3O_4/WS_2: 0.05 g of WS_2 and 0.01 g of $Co(Ac)_2\cdot 4H_2O$ were dissolved in the mixed solution with CH_3CH_2OH and $NH_3\cdot H_2O$, then the mixed solution was heated at 80 ^oC under protection of N_2 atmosphere and kept stirring for 20 h. Then, the black power was collected by filtration and drying at 150 ^oC for 3 h. Finally, the Co_3O_4/WS_2 was obtained.

Synthesis of Co_3O_4/C: 0.05 g of Vulcan-XC72 and 0.01 g of $Co(Ac)_2\cdot 4H_2O$ were dissolved in CH_3CH_2OH and $NH_3\cdot H_2O$ solution, heated at 80 ^oC and kept stirring for 20 h under N_2 atmosphere. After cooling down, the solution was washed to natural and dried at 50 ^oC. Then, the black power was kept at 150 ^oC for 3h in oven. Finally, the Co_3O_4/C was prepared successfully.

Material characterizations: X-ray powder diffraction (XRD) patterns were obtained using an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10^o min^{-1} in the range of 10–80°. XPS experiments were performed on a

Kratos AXIS Ultra DLD system with Al Kα radiation as the X-ray source. SEM was carried out using a Hitachi SU8010 scanning electron microscope operated at an accelerating voltage of 10 kV. HRTEM was achieved using a FEI Talos F200X S/TEM with a field-emission gun at 200 kV.

Electrochemical measurement: The electrochemical measurement system was carried out by CHI-660E in three-electrode system, which contained working electrode (rotating disk electrode), counter electrode (carbon rod) and reference electrode (Hg/HgO). The electrochemical tests were conducted in O_2-saturated 1.0 M KOH electrolyte and the catalyst load was 2.0 mg cm^{-2}. The linear sweep voltammetry (LSV) measurement was carried out at the scan rate of 5 mV s^{-1} in OER and ORR. All potential was calibrated to standard potential according to Nernst equation, which is described as E (vs. RHE)=E(Hg/HgO) +0.098+0.059×pH. The H_2O_2 yield was calculated based on the equation: $H_2O_2\%=200\times\frac{I_{ring}/N}{I_{ring}/N+I_{disk}}$, and the corresponding electron transfer number was evaluated based on the equation: $n=4\times\frac{I_{disk}}{I_{disk}+I_{ring}/N}$. I_{ring} and I_{disk} are the ring and disk current densities, respectively. N is the collection efficiency of the RRDE, which was measured in 0.1M KNO_3 electrolyte with additional $K_3[Fe(CN)_6]$.

Zn-air battery measurement: The catalyst was sprayed on carbon paper, which was used as cathode and the load was 2 mg cm^{-2}. Zn plate played the role of anode and nickel foam was used as current collector. The filled electrolyte between the catalyst and Zn plate was 6 M KOH containing 0.2 M Zn $(CH_3COO)_2$. Differently, in terms of the all-solid-state zinc-air battery, the electrolyte was PVA membrane. All zinc-air battery measurements were recorded by Arbin testing system.

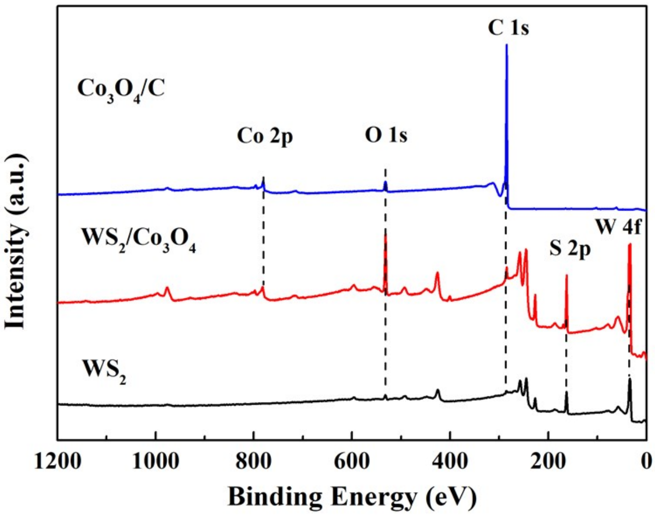

Figure S1. XPS survey scan of WS_2, Co_3O_4/WS_2 and Co_3O_4/C electrocatalysts.

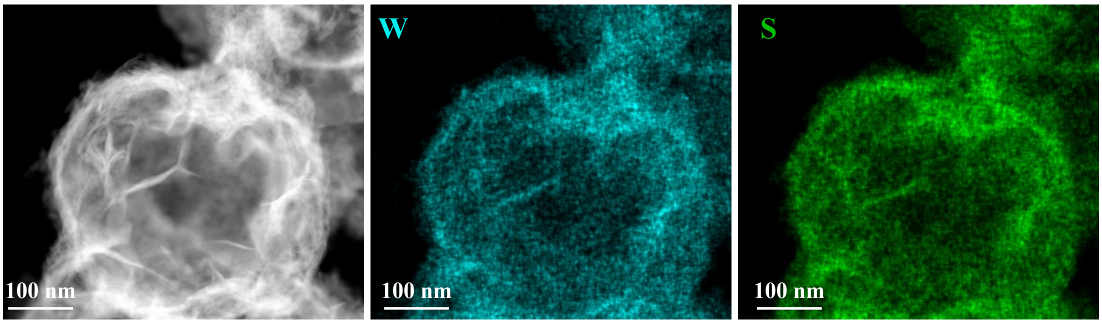

Figure S2. HAADF-STEM image and EDS mapping of WS_2 electrocatalyst.

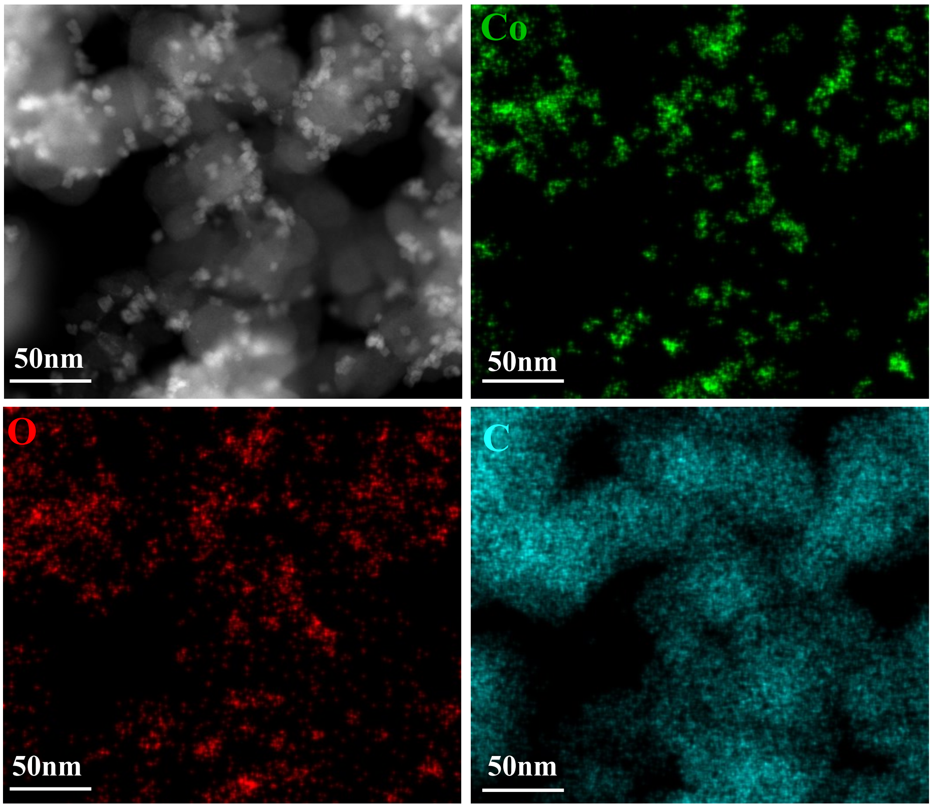

Figure S3. HAADF-STEM image and EDS mapping of Co_3O_4/C electrocatalyst.

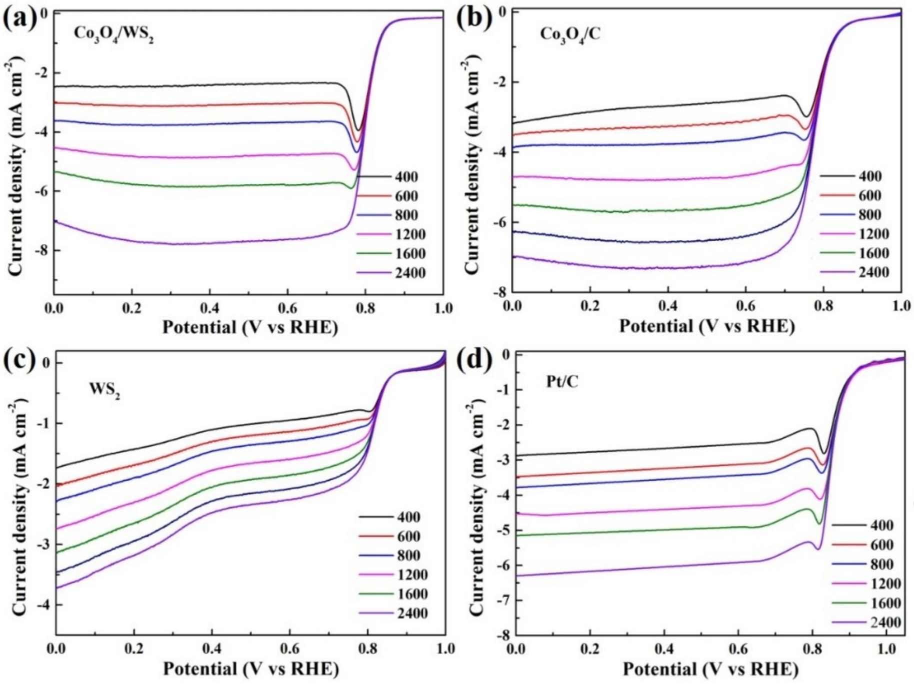

Figure S4. LSV curves of (a) Co_3O_4/WS_2, (b) Co_3O_4/C, (c) WS_2 and (d) Pt/C with different scan rates.

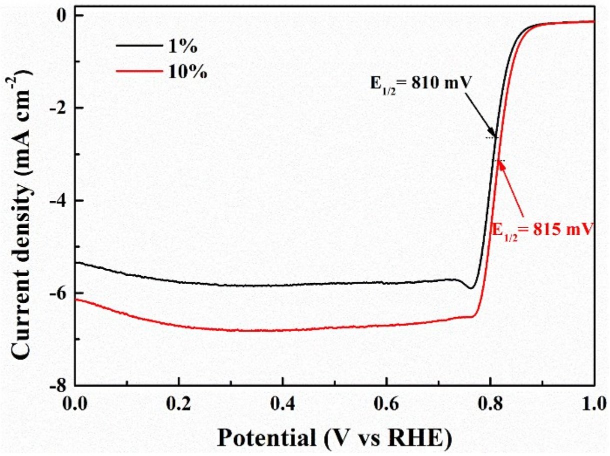

Figure S5. LSV curves of Co_3O_4/WS_2-1wt% and Co_3O_4/WS_2-10wt% electrocatalysts recorded at 1600 rpm.

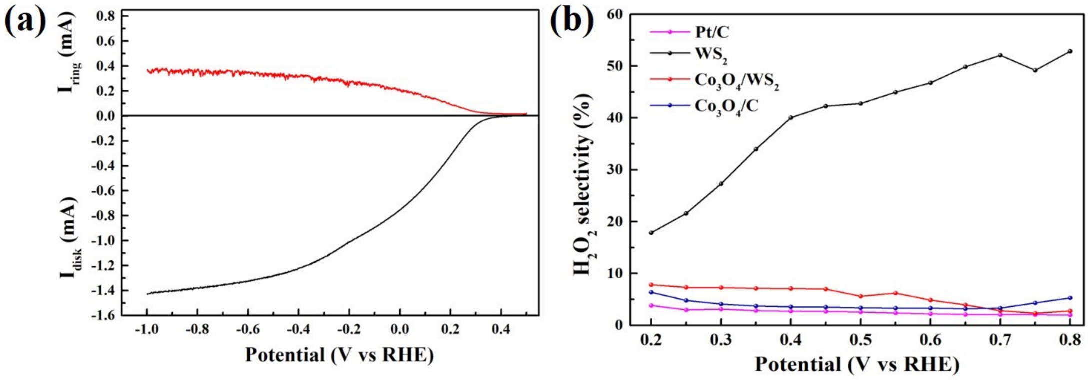

Figure S6. (a) The RRDE polarization curves and (b) the H_2O_2 selectivity of different catalysts.

Prior to H_2O_2 assessment, the collection efficiency (N) was evaluated in 0.1 M KNO_3 electrolyte with additional $K_3[Fe(CN)_6]$ and calculated as 0.26 (**Fig. S6a**).

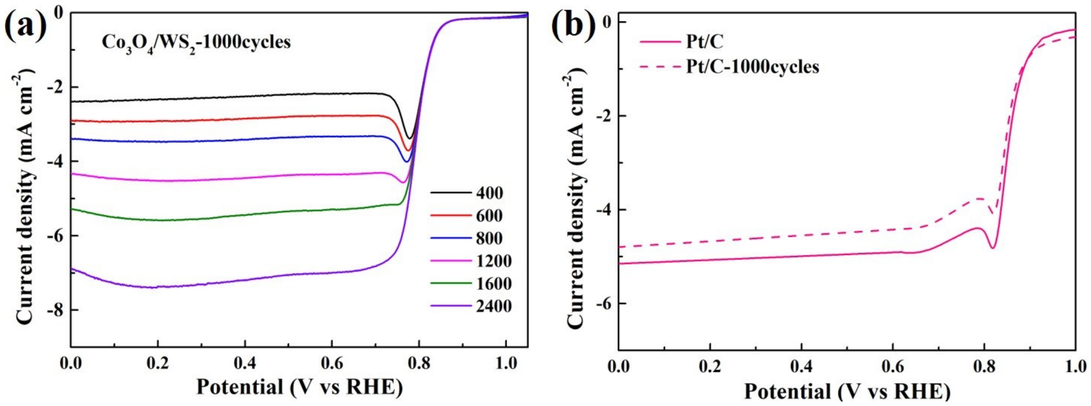

Figure S7. (a) LSV curves of Co_3O_4/WS_2 after 1000 cycles with different scan rates and (b) LSV plots of Pt/C before and after 1000 cycles.

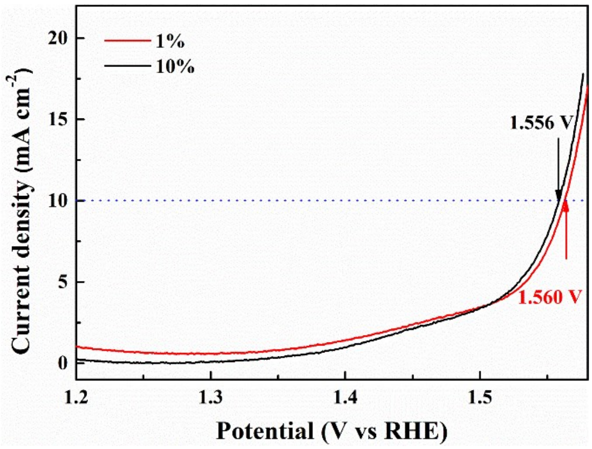

Figure S8. OER performance of Co_3O_4/WS_2-1wt% and Co_3O_4/WS_2-10wt% electrocatalysts.

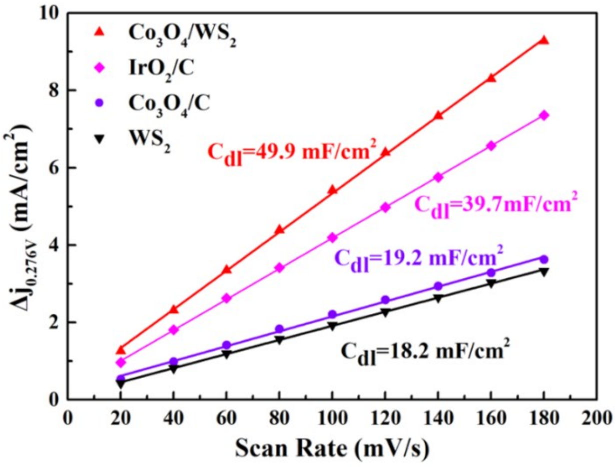

Figure S9. Calculated double-layer capacitances (C_{dl}) of different catalysts.

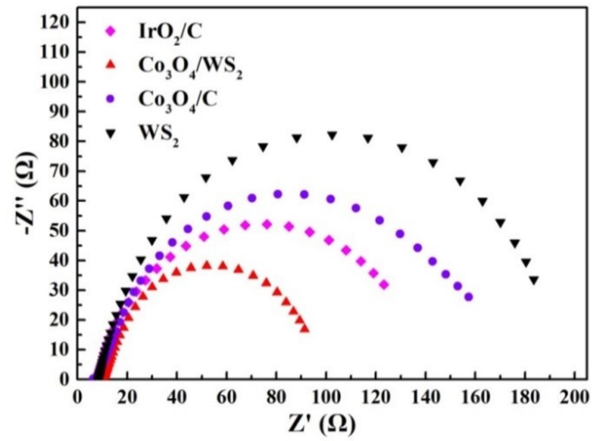

Figure S10. Electrochemical impedance spectra (EIS) plots of different catalysts.

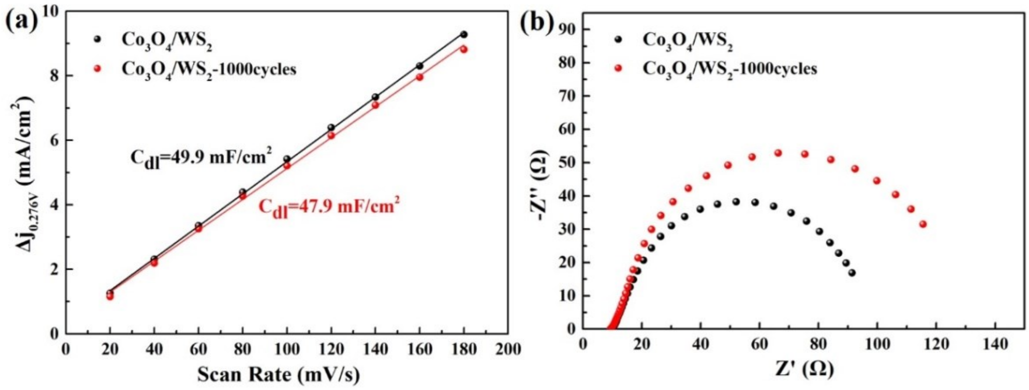

Figure S11. (a) Calculated double-layer capacitances (C_{dl}) and (b) electrochemical impedance spectra (EIS) of Co_3O_4/WS_2 before and after 1000 cycles.

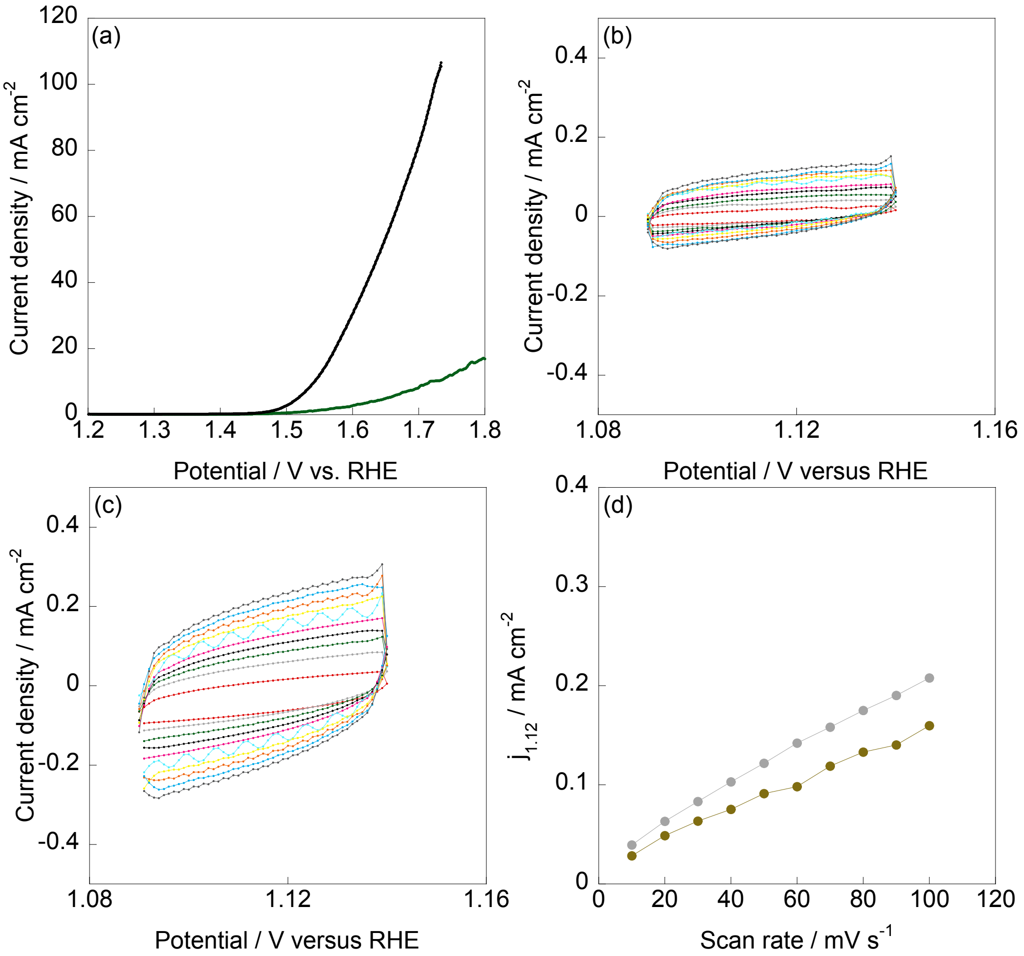

Figure S12. (a) LSV curves, CV curves (b, c) and ECSAs (d) of IrO_2/C before and after 1000 cycles.

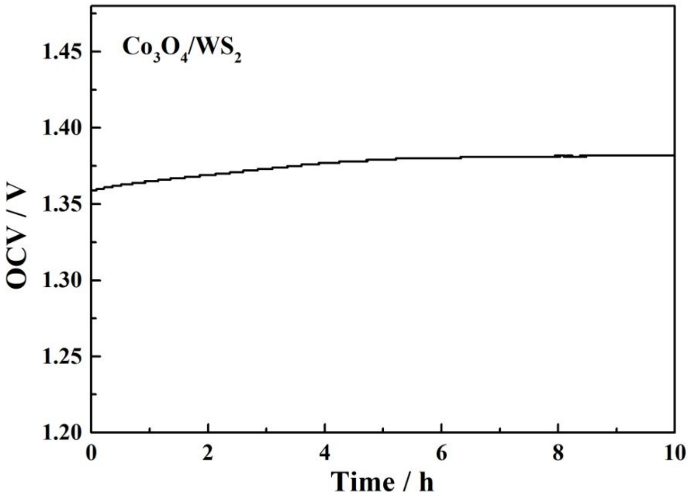

Figure 13. The open circuit voltage of rechargeable zinc-air battery fabricated from Co_3O_4/WS_2.

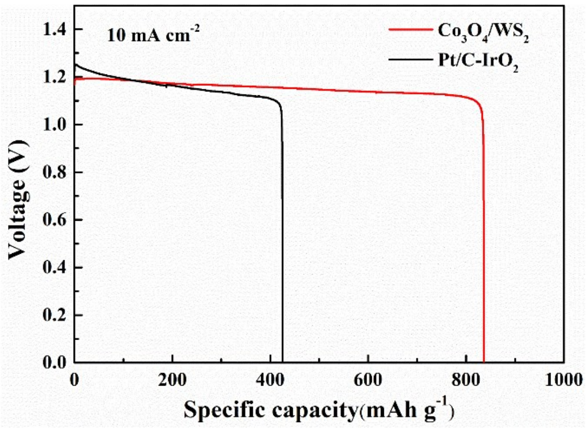

Figure S14. Specific activities of Co_3O_4/WS_2 and Pt/C-IrO_2 tested with 10 mA cm^{-2}.

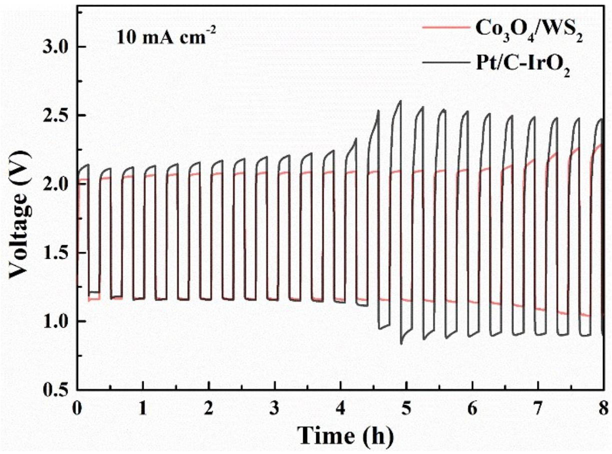

Figure S15. Cyclic performance of Co_3O_4/WS_2 and Pt/C-IrO_2 at 10 mA cm^{-2}.

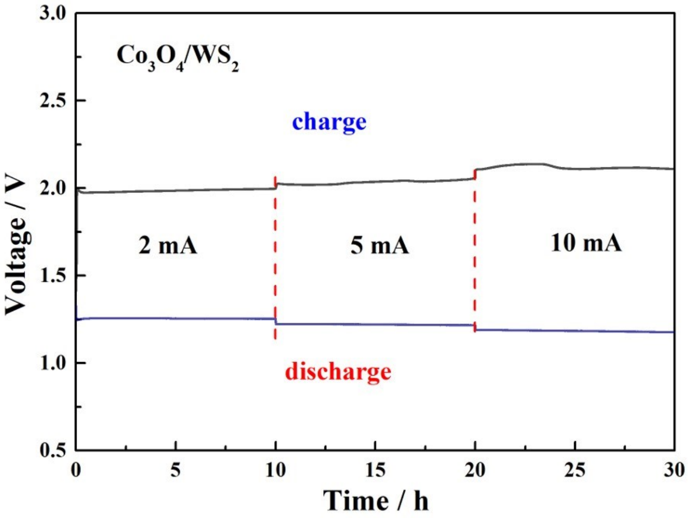

Figure S16. The discharge-charge potential curves at different current density of Co_3O_4/WS_2.

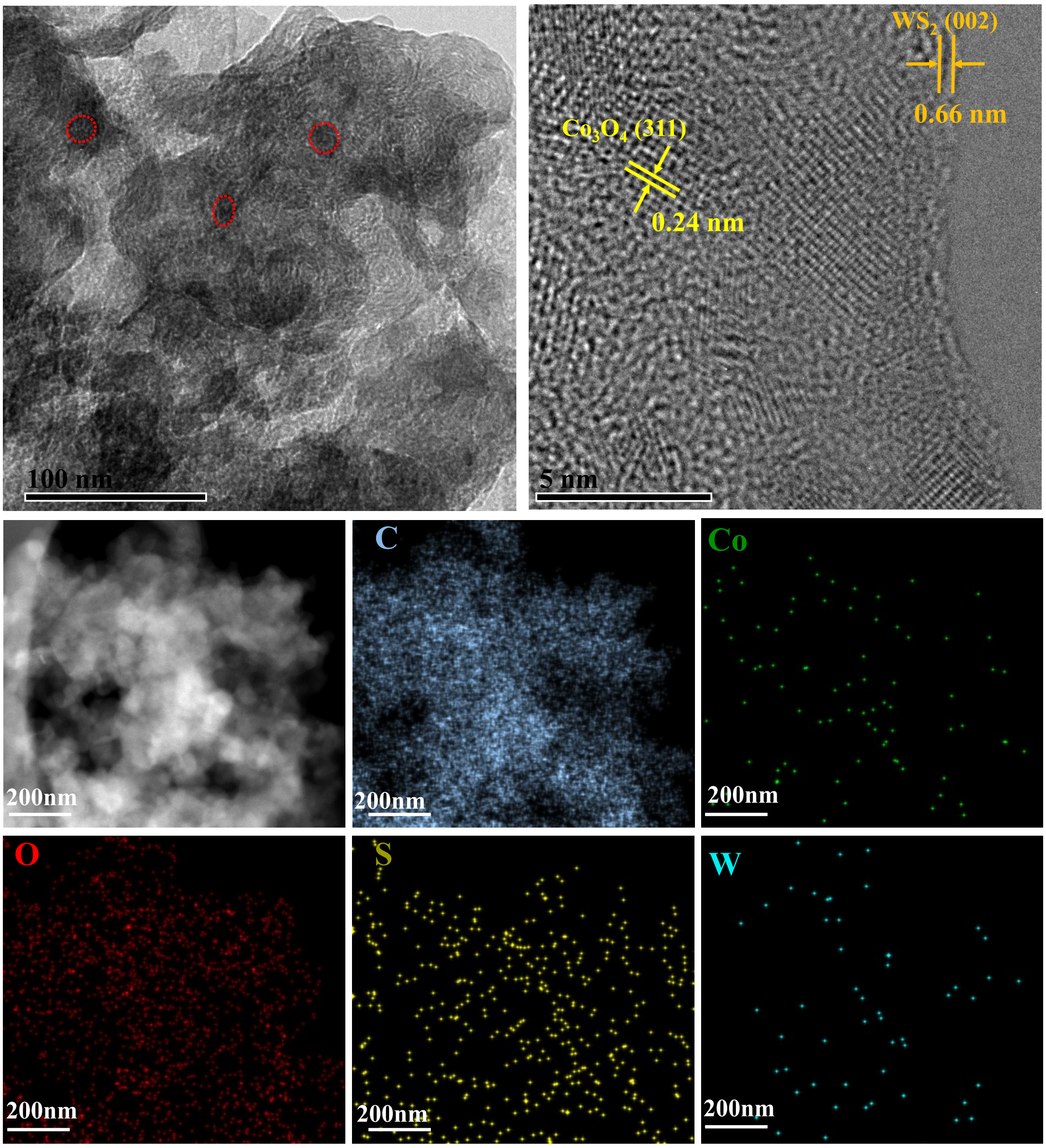

Figure S17. TEM image and EDS mapping of Co_3O_4/WS_2 after stability test.

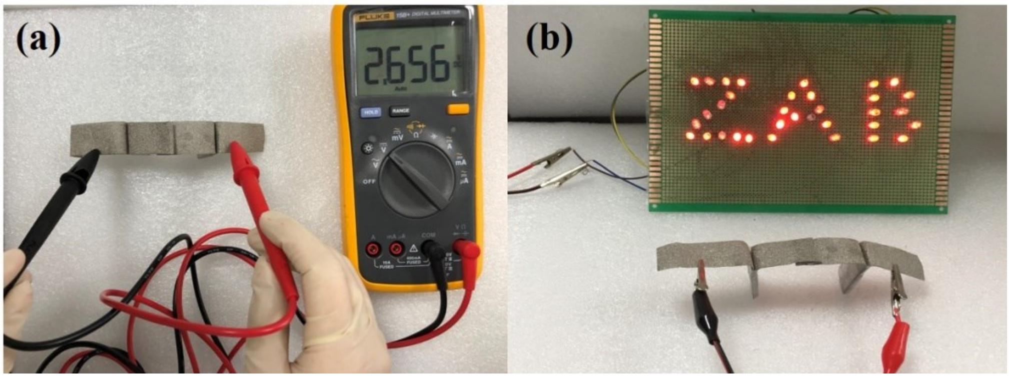

Figure S18. (a) Open circuit voltage and (b) light bulb test of two all-solid-state zinc air batteries in series of Co_3O_4/WS_2.

Meaningfully, two batteries can light LED bulbs shown in **Fig. S18,** suggesting the potential applications of the constructed powerful rechargeable ZABs.