Supporting Information

A deeply-rechargeable zinc anode with pomegranate-inspired nanostructure for high-energy aqueous batteries

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Materials and Methods

Microemulsion-based assembly of ZnO nanoparticles into clusters. The nanoparticles of ZnO (ZnONPs, Aldrich, 100 mg) were dispersed in 2 mL distilled water by ultrasonication for 5 min, and then the emulsion was mixed with 8 mL1-octadecene (ODE, Aldrich) solution containing 0.5 wt% of emulsion stabilizer (amphiphilic block copolymer, Hypermer 2524, Croda USA) and homogenized at 7000 rpm for 1 min. The water in the mixture was evaporated at 92~98 °C until no water vapor was observed. Then the ZnO clusters were collected by centrifugation for 5 min at 1500 rpm and washed with cyclohexane twice. The cyclohexane was dried on the hotplate at 80 °C. The final powder was calcined at 400 °C for 2 hours and 600 °C for 1 h in air to remove the organics and condense the ZnO clusters.

Carbon coating on Clusters. The powder of ZnO clusters (100 mg) was dispersed in 100 mL of water in 200 mL beaker, and 1000 μL Tris buffer pH 8.5 was added into the beaker while it was stirred at 200rpm·min^{-1}. The dopamine (200mg, Aldrich) was added to the mixture, which was then stirred for 24 hours. The Zn-pome was collected by centrifugation at 1500 rpm and washed 3 times with distilled water. The water was subsequently removed by heating at 80 °C. The final Zn-pome was carbonized at 600°C for 1 hour with a heating rate of 5 °C/min in argon atmosphere.

Characterization. The morphology analysis of bare ZnO, ZnO Clusters, and Zn-pome was carried out using scanning electron microscopy (SEM, Hitachi SU 8230). The morphology of Zn-pome and the carbon shell after etching the ZnO cluster was determined using transmission electron microscopy (TEM, Hitachi HT7700). The cross-sectioned images of clusters after being etched in 1M HCl were generated using FEI Nova Nanolab 200 FIB/SEM that included SEM imaging and Focus Ion Beam (FIB) milling. The X-ray diffraction pattern (XRD, Panalytical XPert PRO Alpha-1) for bare ZnO, ZnONPs@C, and Zn-pome were carried out with CuK-Alpha radiation. The X-ray photoelectron spectroscopy (XPS) was measured with AlK-Alpha (Thermo K-alpha). XPS survey spectra and high-resolution spectra of Zn2p, O1s, and C1s were measured. The weight percentage of ZnO in Zn-pome was determined from the weight loss curves measured under air atmosphere on a thermogravimetric analysis instrument (TGA, TA instrument, Q500) with a heating rate of 5 °C/min to 850 °C. The specific Brunauer–Emmett–Teller surface areas and pore size distribution were determined by physisorption (BELSORP-MAX, Microtrac BEL Japan, Inc.). The dissolved concentration of bare ZnO, ZnONPs@C, Zn-pome in 4M KOH electrolyte was measured with an inductively coupled plasma (ICP) measurement: three samples with the same amount of active material were immersed into 4 M KOH for 5 minutes, and the supernatant after centrifugation was measured. The ICP samples were filtered with 0.2 μm Acrodisc IC PES filters and diluted 100 times in ICP Matrix Solution.

Electrode preparation. 151 mg synthesized Zn-pome was gently ground in a mortar and transfered into a 4 mL vial with 0.5 g N-Methyl-2-pyrrolidone (NMP, Aldrich), then the 1.2 g NMP solution containing PVDF (MTI, ~ 10 wt% of PVDF) was added to the sample and stirred for 30 minutes. The slurry was then cast onto Sn foil (Alfa) with a Doctor's blade and dried at 80 °C for 30 minutes.

Electrochemistry. 2032 coin cells were assembled under ambient environment, with Zn-pome anode, $Ni(OH)_2$ cathode obtained from commercial Zn-Ni batteries (PowerGenix), and a separator (GF 6, Whatman). The aqueous electrolyte contains 4 M KOH (Aldrich), 2 M K_2CO_3 (Aldrich) and 2 M KF (Aldrich). The control cells were assembled using the same process as Zn-pome anode batteries, just with the Zn-pome anode replaced by the bare ZnO anode. The cells were charged and discharged at 1 C for comparison between bare ZnO and Zn-pome, and the performances of the 5 C rate discharge and self-discharge were investigated respctively.

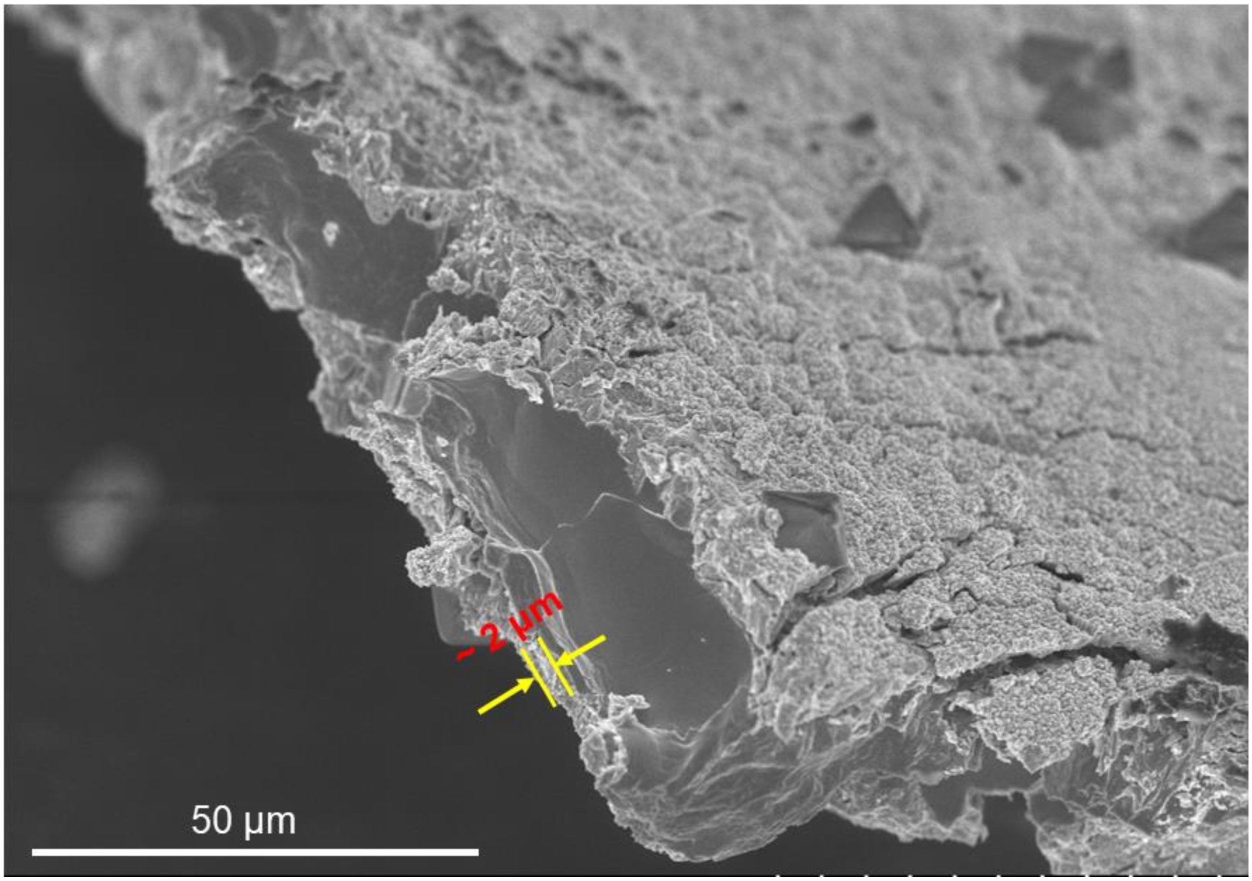

Fig S1. Cross-sectional SEM image of Zn mesh with a ZnO passivation layer formed on it after discharging the Zn mesh under 1 mA with 100 µL electrolyte consists of 2 M KF, 2 M K_2CO_3 and 4 M KOH. The passivation layer is approximately 2 µm.

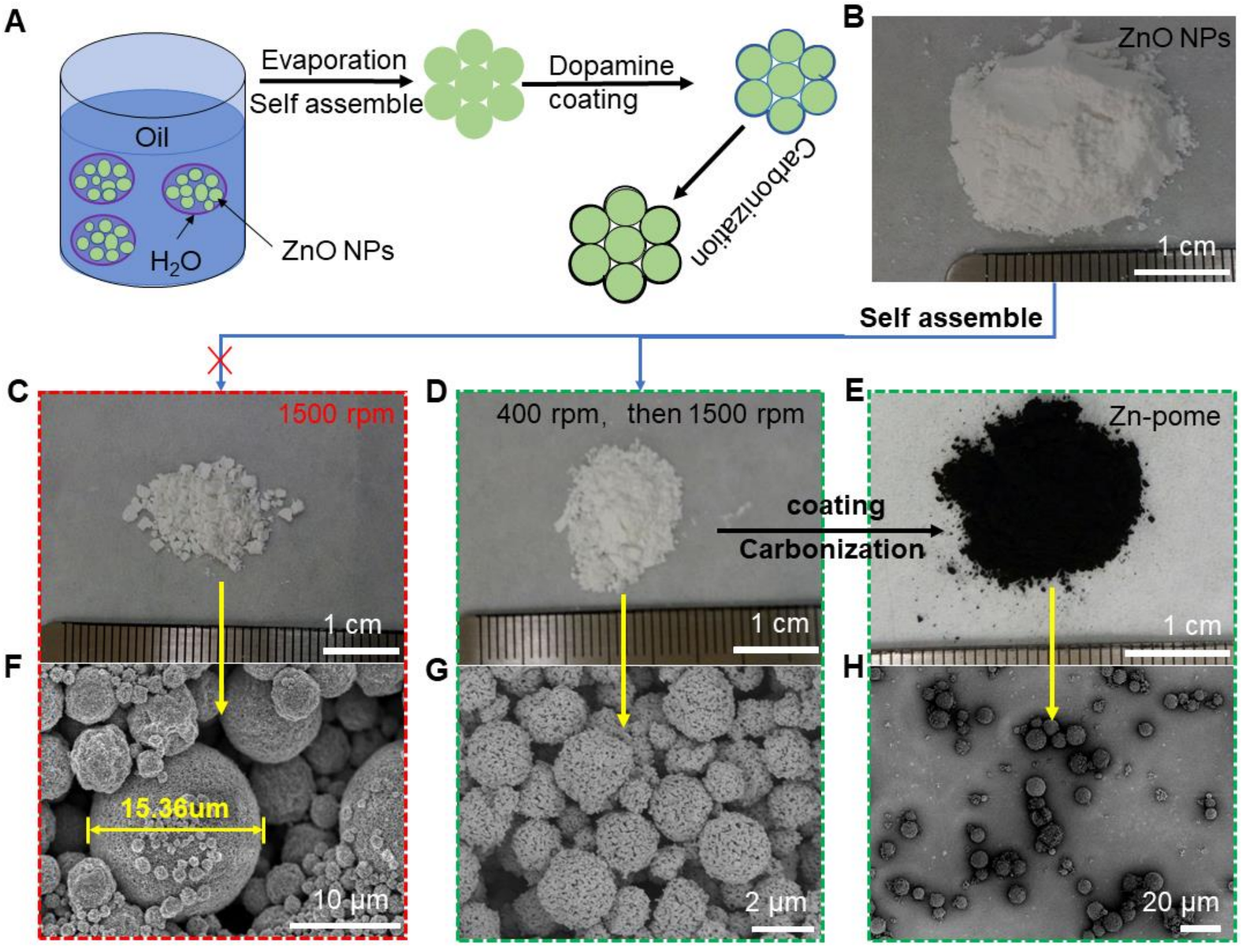

Fig S2. Synthesis of Zn-pome. (A) The Zn-pome were prepared by a bottom-up microemulsion approach. (B) A picture of ZnO NPs. (C,F) A picture and a SEM image of ZnO clusters collected from centrifugation at 1500 rpm for 5 min. The size is not uniform. (D,G) A picture and a SEM image of ZnO clusters obtained by first centrifuging at 400 rpm for 1 min to remove large clusters, and then centrifuging at 1500 rpm for 5 min. (E,H) A picture and a SEM image of Zn-pome synthesized using Zn clusters shown in D and G.

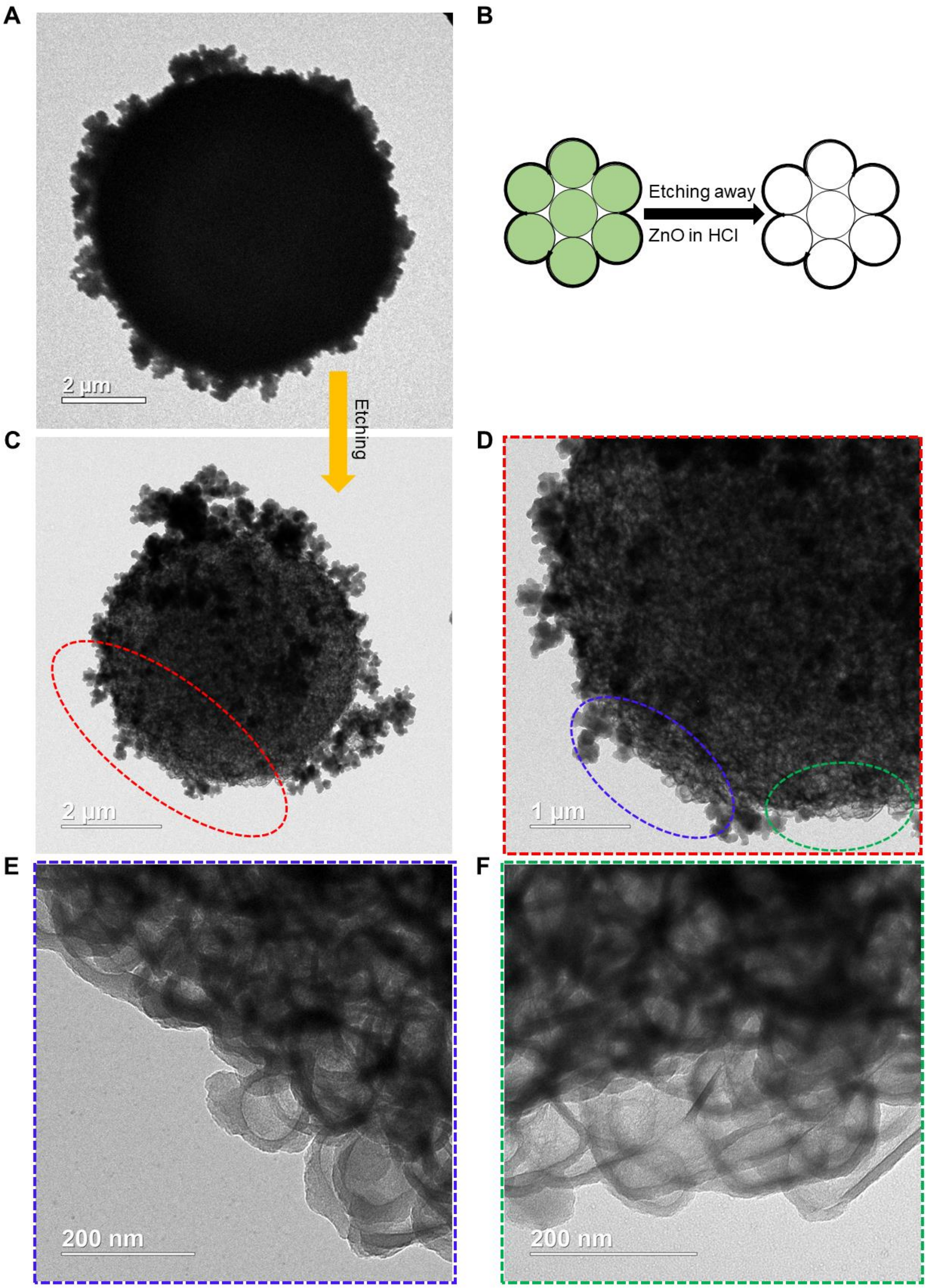

Fig S3. (A) TEM images of Zn-pome. (B) Schemtic of etching ZnO. (C-F) TEM images of Zn-pome after etching away ZnO in 1 M HCl.

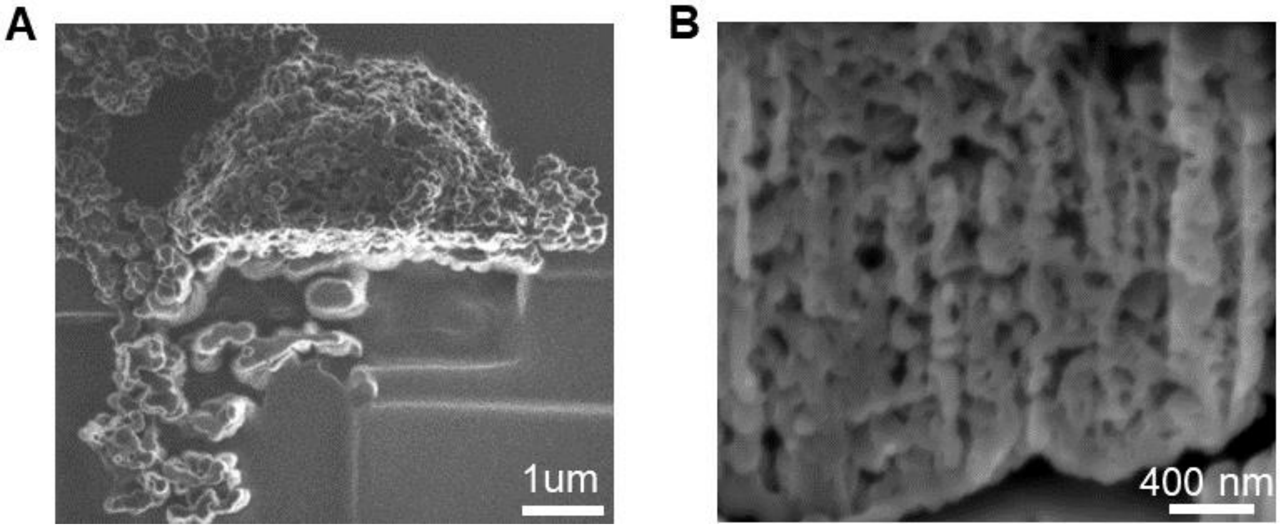

Fig S4. Focus Ion Beam (FIB) milling of Zn-pome. (A) Top-view image of Zn-pome after FIB milling. (B) Cross-section image of Zn-pome after FIB milling.

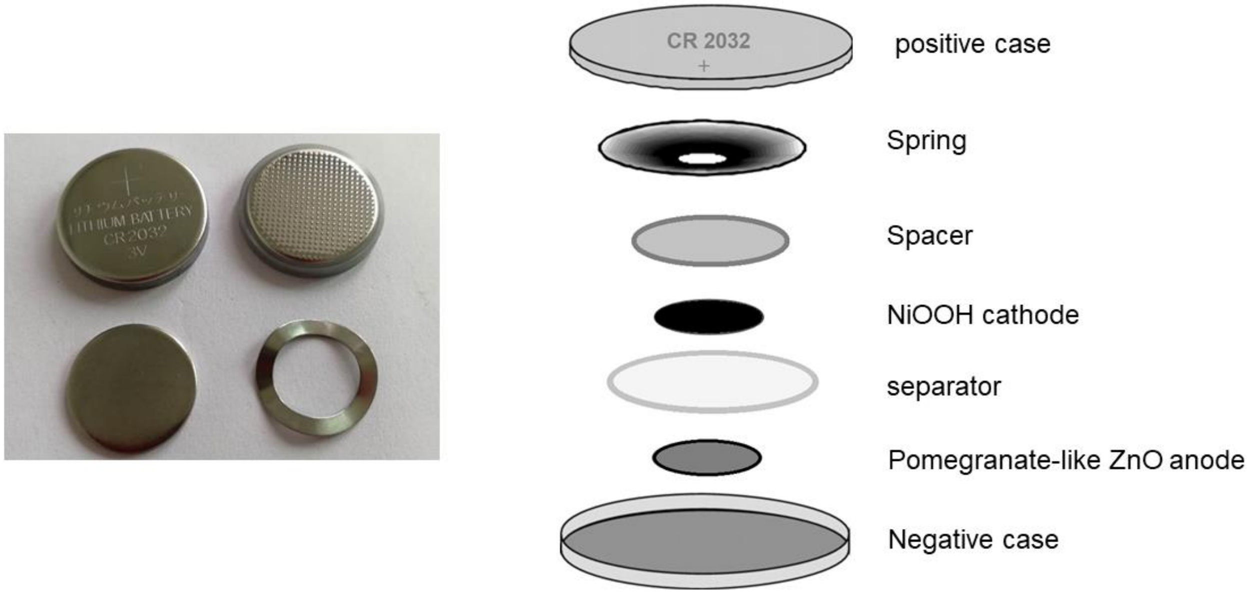

Fig S5. Picture of CR2032 coin cell cases (left) and schematic of coin cell components and their arrangement used in this work (right).

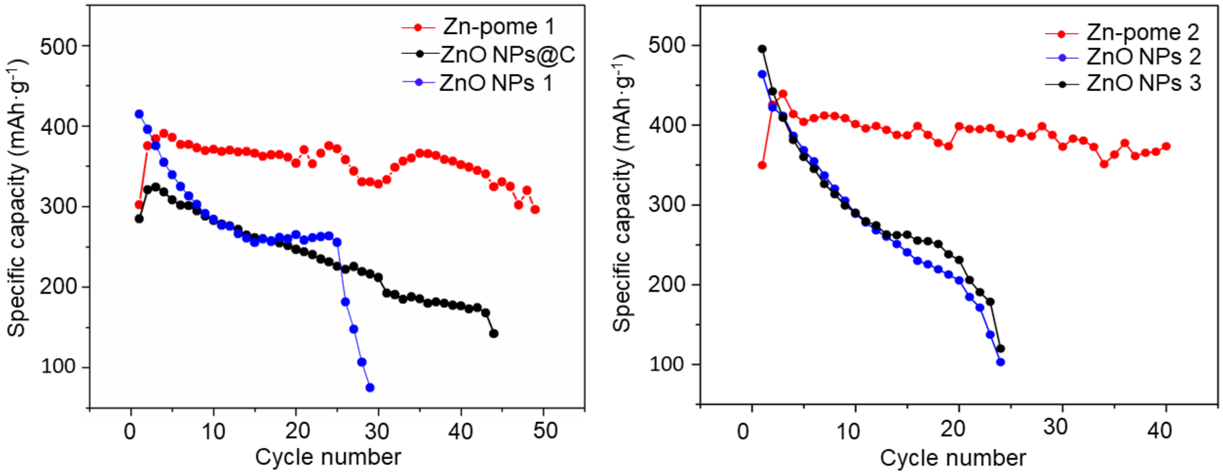

Fig S6. (left) Specific capacity of Zn-pome, ZnO NPs@C and ZnO NPs. (right)Additional battery cycling data of bare ZnO and Zn-pome anodes (1 C rate).

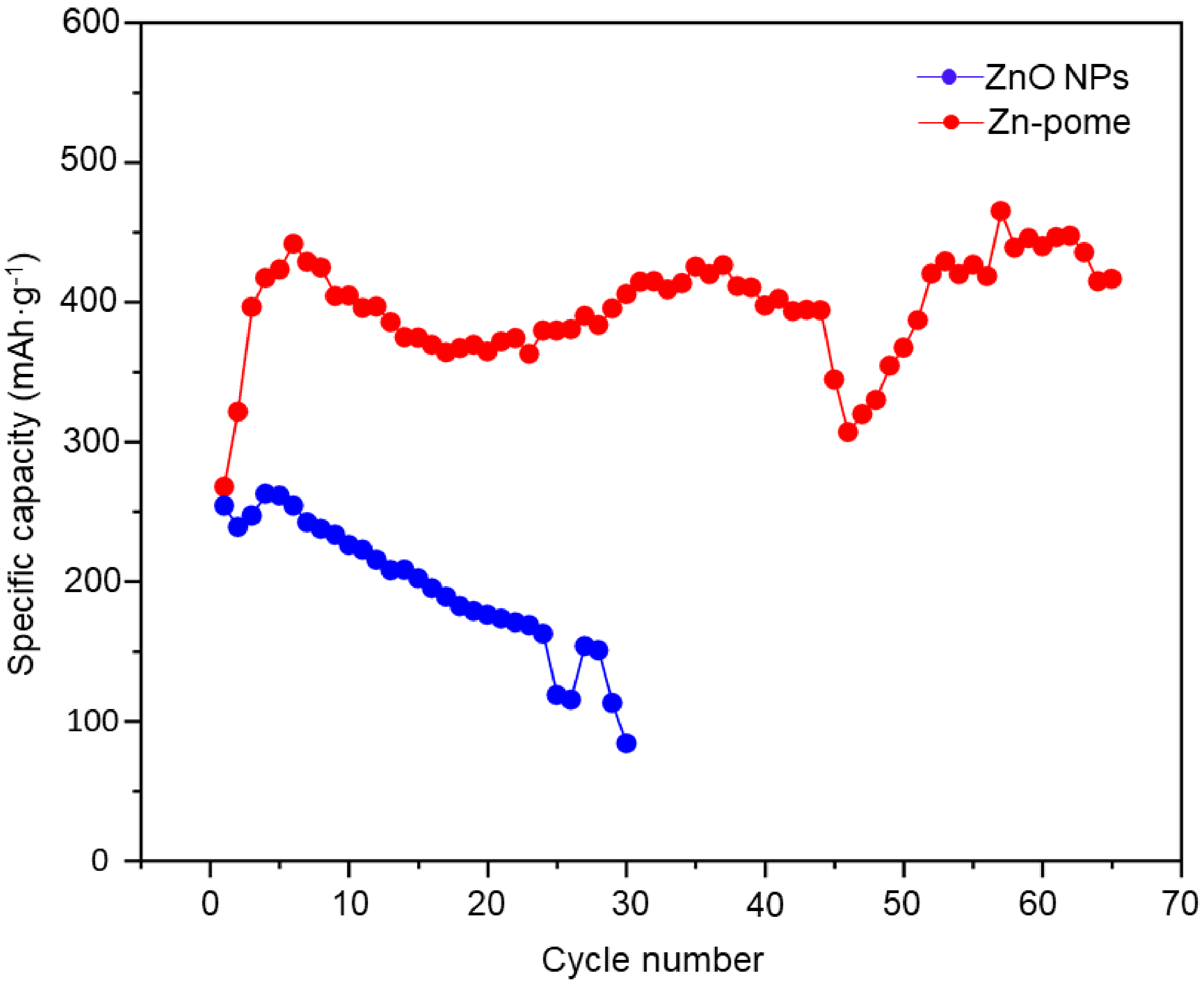

Fig S7. The performance of bare ZnO and Zn-pome anodes at 5 C discharge rate.

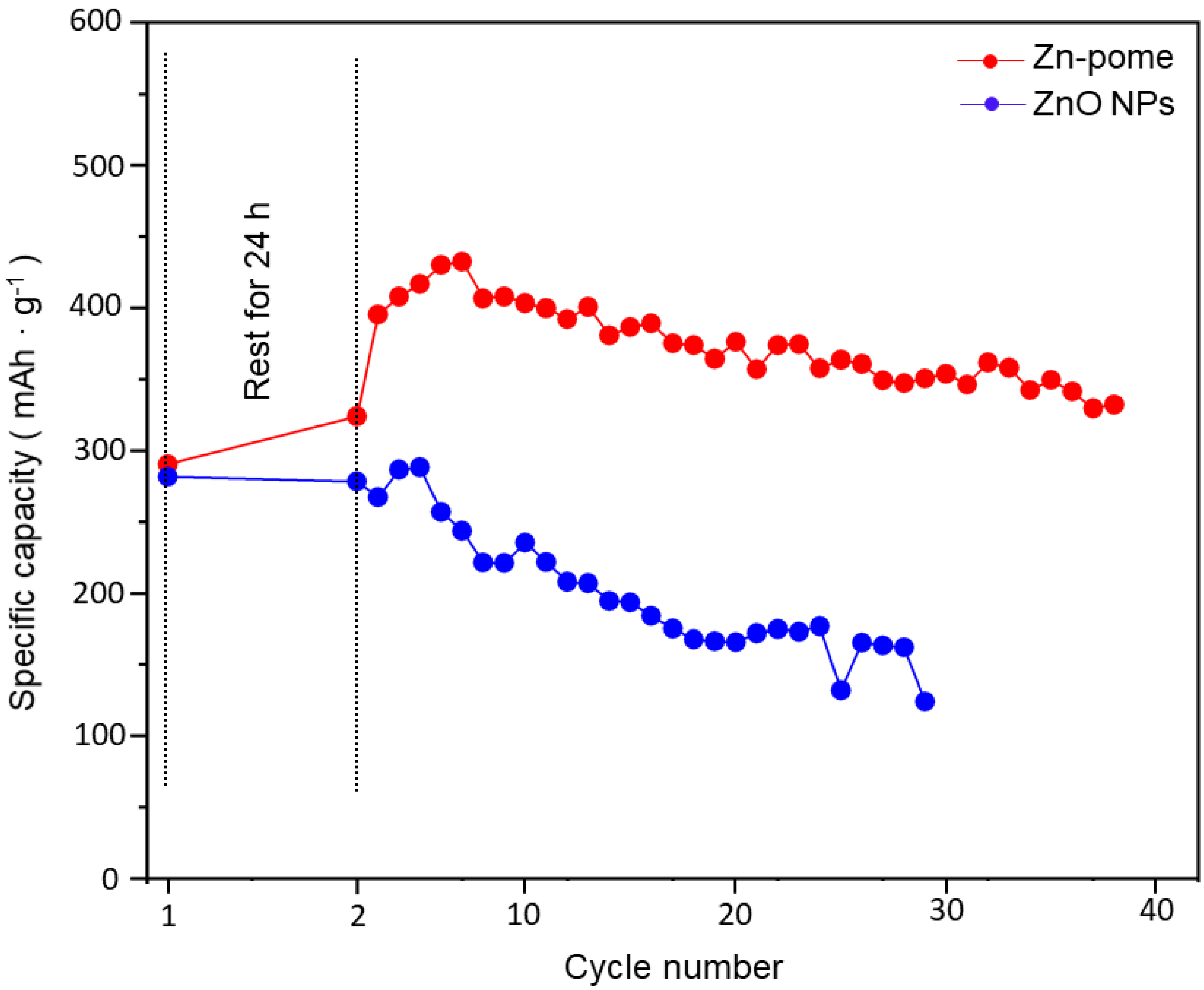

Fig S8. The cycle performance of bare ZnO and Zn-pome anodes (charged at 1 C, discharged at 5 C), after resting for 24 hours followed by the first cycle at 0.5 C.

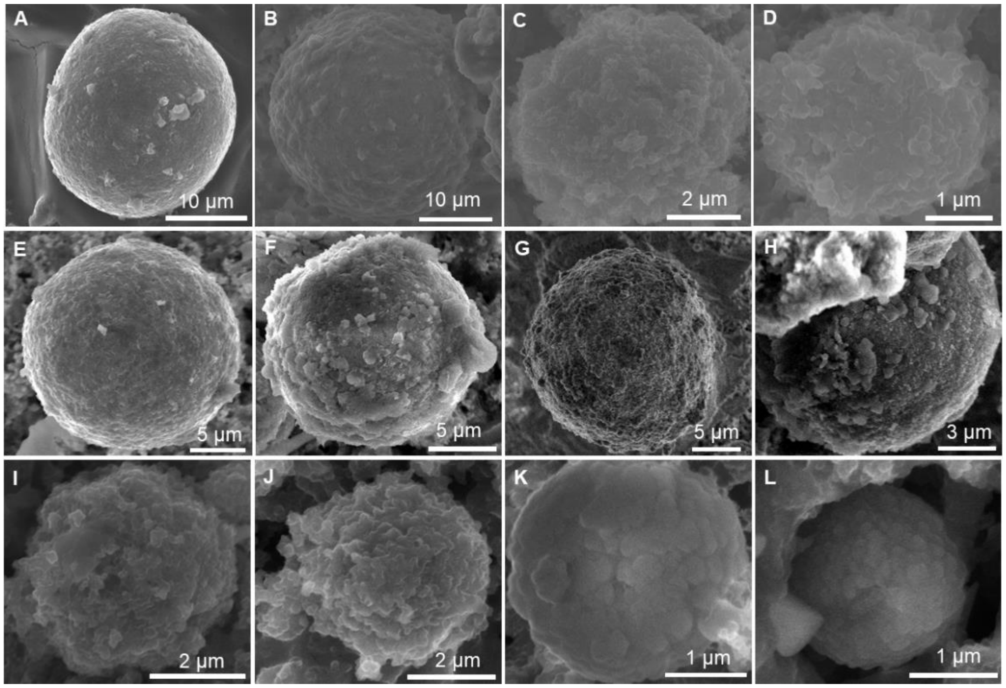

Fig S9. SEM images of Zn-pome anode after cycling at 1C. (A-D) after cycling 10 cycles. (E-L) after cycling 20 cycles.