Electronic Supplementary Information

Guiding Uniform Zn deposition by cocoons for long-life Zn metal batteries

Yu Xia,[a] Xing Xin,[a] Yu Pan,[a] Ping Zhang,[c] Fenghua Liu*[bc] and Xing Li*[a]

[a] *School of Physical Science and Technology, Ningbo University, Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province, Ningbo 315211, China*

[b] *Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Science, Ningbo, 315201, P.R. China.*

[c] *Xuyi County Attapulgite Application Technology R&D and Achievement Transformation Center, Xuyi, 211700, P.R. China.*

Experimental Section

Preparation of silkworm

The silk cocoons were washed in an ultrasonic wave by deionized water and ethyl alcohol for more than three times. After that, the cocoons were flattened and dried in oven for overnight. The cocoon-800 was heated in a tube furnace with continuous nitrogen from the room temperature to 600 ℃ for 60 minutes at a rate of 3 ℃ min^{-1} and then to 800 ℃ for 120 minutes at a rate of 3.33 ℃ min^{-1}. The cocoon-400 were fabricated under the same conditions. The cocoon-400 was heated from the room temperature to 200 ℃ for 60 minutes at a rate of 3.33 ℃ min^{-1} and then 400 ℃ for 120 minutes at a rate of 3.33 ℃ min^{-1}. At last, all the samples were cut into wafers with the diameter of 16 mm.

Material Characterization

X-ray power diffraction (XRD) was carried out on a Bruker D8 Focus X-ray diffraction with Cu-Kα radiation (λ=1.5406 nm). The microscopic morphology of the prepared silk cocoon slices and energy dispersive spectrometry (EDS) were obtained on Hitachi S4800 scanning electron microscopy (SEM). Thermogravimetric analysis of silk cocoon was measured on a SIITG/GTA 7300 in a nitrogen atmosphere at a heating rate of 15 ℃ min^{-1} from room temperature to 900 ℃.

Electrochemical Measurements of Symmetrical Zn|$ZnSO_4$|Zn Cells

The bare Zn sheets were cut into disc-shaped electrodes (Φ=16 mm) and the thickness is 100 μm. The Zn|$ZnSO_4$|Zn cells were using filter paper (Φ=19 mm) as separator and 1M $ZnSO_4$ aqueous solution as electrolyte to assemble 2032 coin-type cells. The prepared silk cocoon slices were placed on the bare Zn plates besides negative electrode shell and its thickness is about 140 μm. The batteries were tested at

different current densities between 0.25 mA cm^{-2} and 0.5 mA cm^{-2} to evaluate the electrostripping/plating behavior and cycling stability of Zn sheets using a LAND-CT2001A battery test system (Jinnuo Wuhan Corp, China).

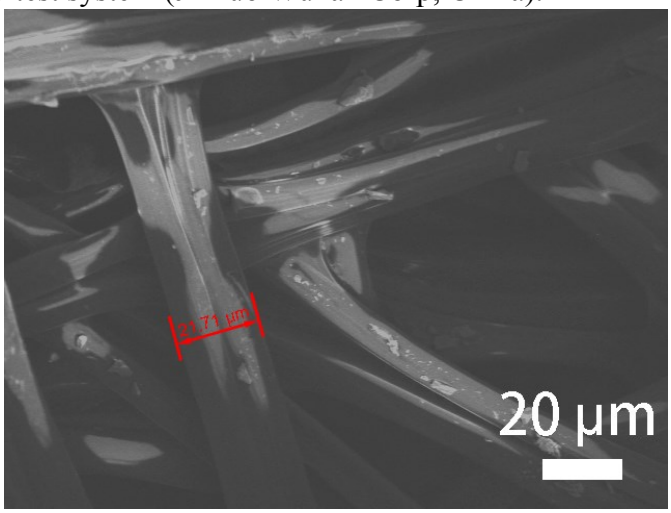

Figure S1 The SEM image of original silk cocoons without heat treatment.

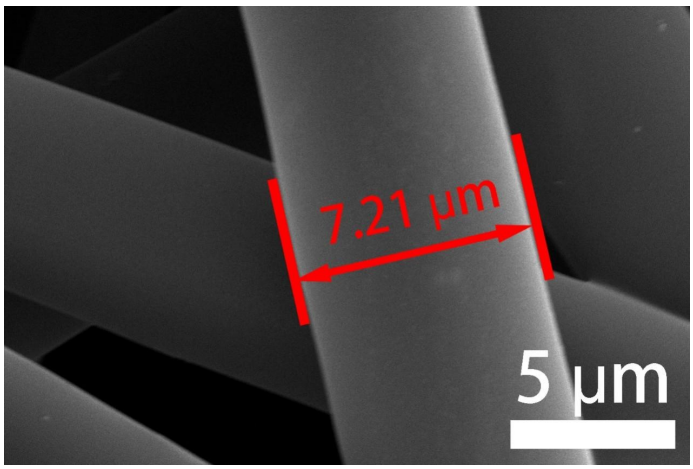

Figure S2 The SEM image of silk cocoons carbonized under the heat treatment of 800 ℃ (cocoon-800) and the diameter is about 7.21 μm.

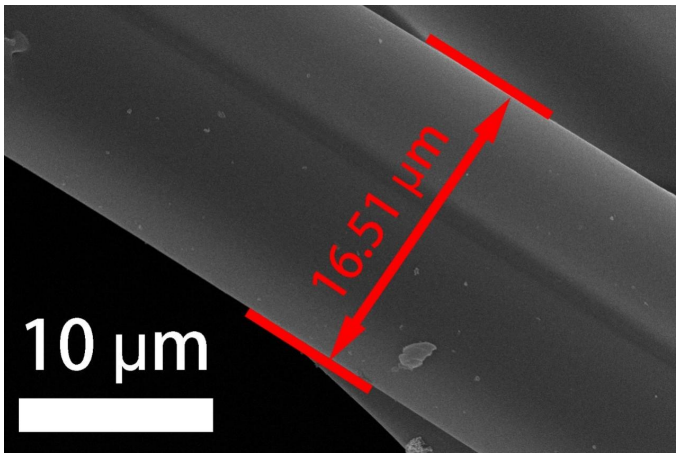

Figure S3 The SEM image of silk cocoons carbonized under the heat treatment of 400 ℃ (cocoon-400) and the diameter is about 16.51 μm.

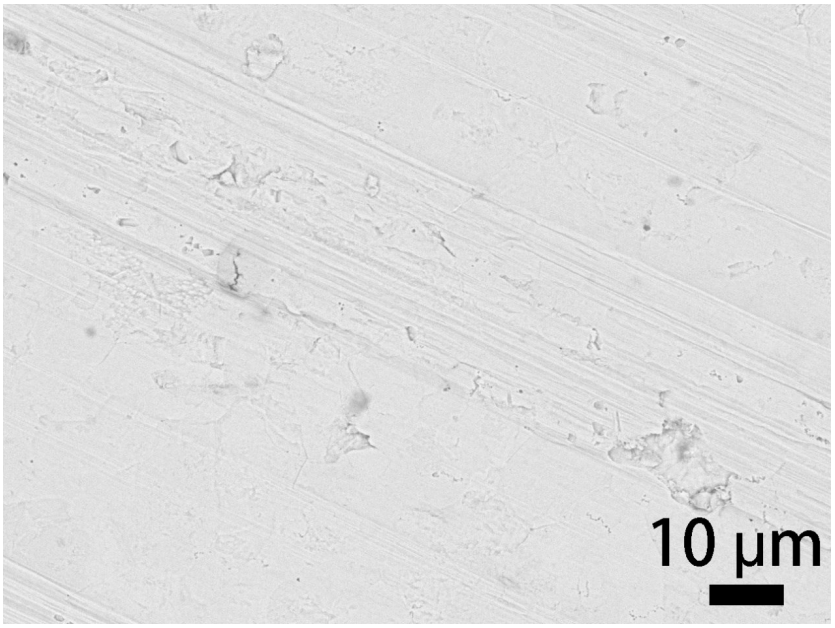

Figure S4 The SEM image of the surface of Zn plate.

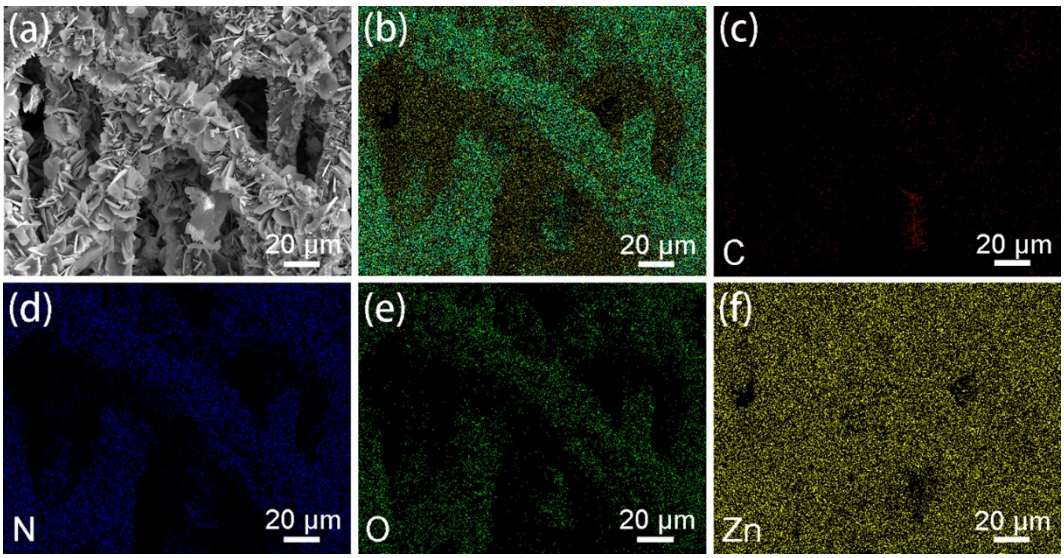

Figure S5 The elemental mapping of the cocoons at the temperature of 800 ℃ after cycling in ZBs-800.

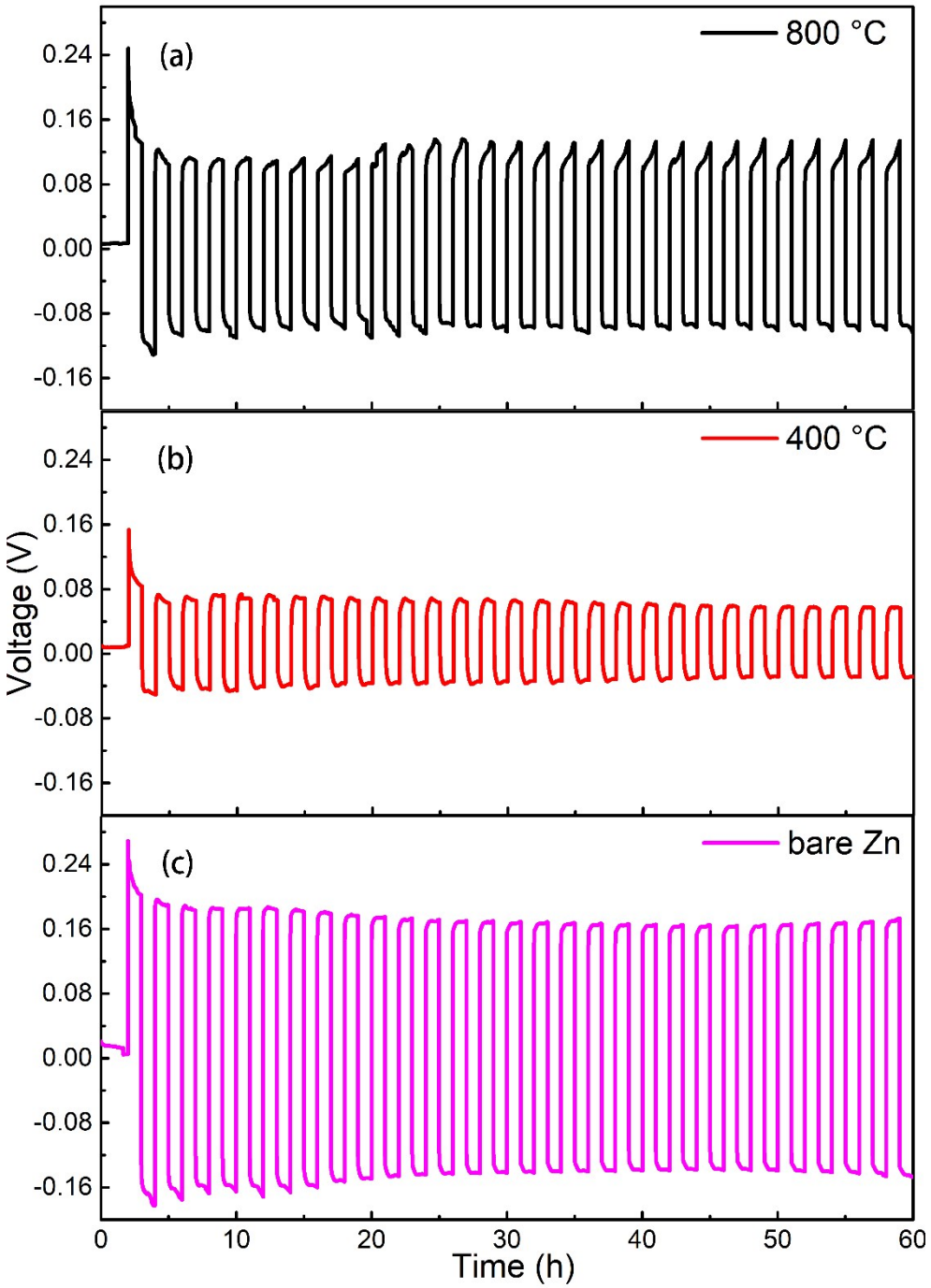

Figure S6 Galvanostatic cycling performances of Zn|$ZnSO_4$|Zn symmetric cells contained fabricated cocoon with the sintered temperature of (a) 800 ℃, (b) 400℃ and (d) bare Zn at a current density of 0.25 mA cm^{-2} after 30 cycles.

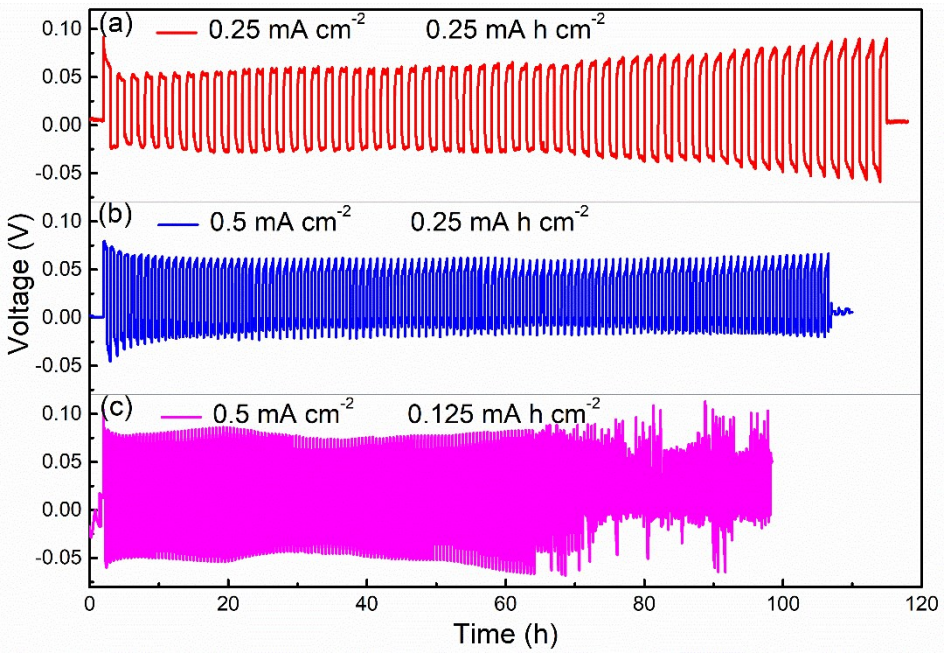

Figure S7 Galvanostatic cycling performances of Zn|$ZnSO_4$|Zn symmetric cells contained fabricated cocoons at 800 ℃ with different current density and capacity density: (a) 0.25 mA cm^{-2}, 0.25 mA h cm^{-2}, (b) 0.5 mA cm^{-2}, 0.25 mA h cm^{-2} and (c) 0.5 mA cm^{-2}, 0.125 mA h cm^{-2}.

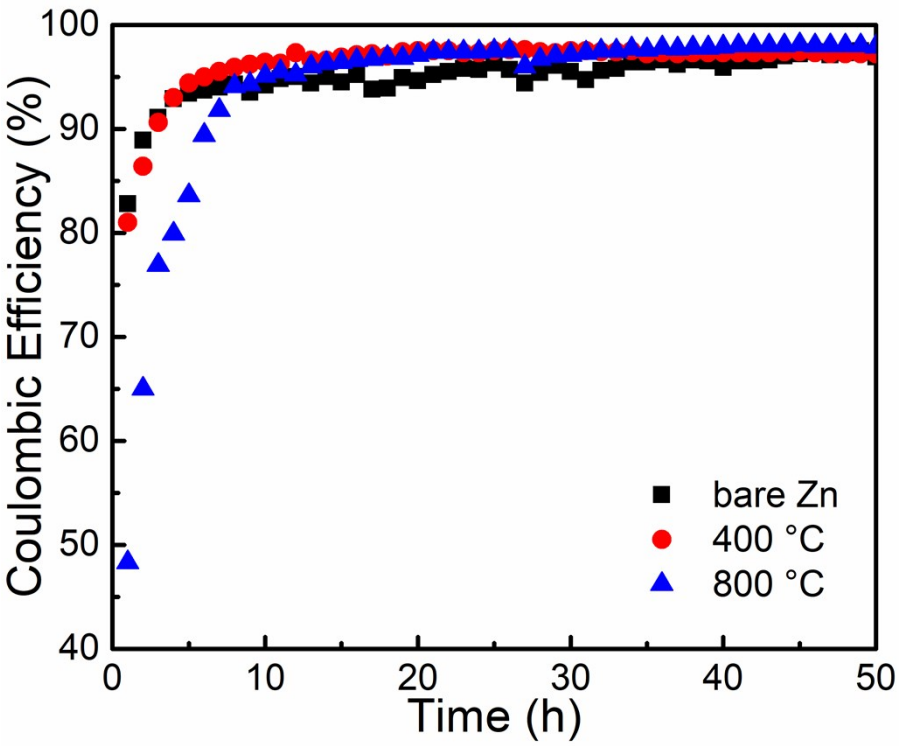

Figure S8 Coulombic efficiencies of Zn|Cu batteries without cocoon and with cocoons under different heating process at a current density of 0.25 mA cm^{-2}.

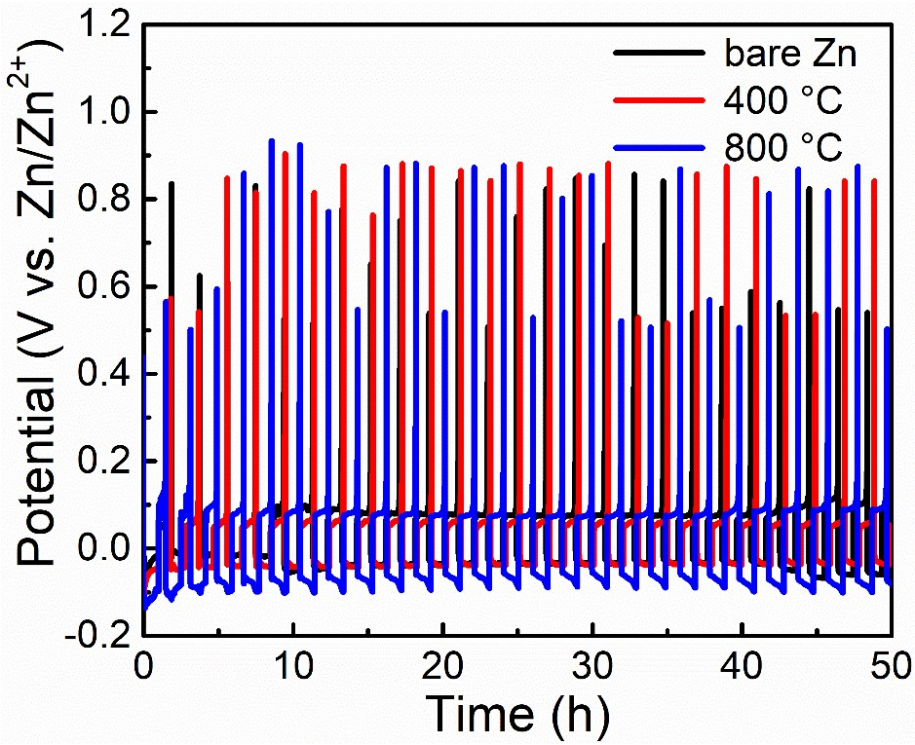

Figure S9 Voltage profiles of charge/discharge process of Zn|Cu batteries without cocoon and with cocoons under different heating process at a current density of 0.25 mA cm^{-2}.