

Supporting Information

Fast production of zinc-hexamethylenetetramine complex microflowers as advanced sulfur reservoir for high-performance lithium-sulfur batteries

Xiaoyuan Dou,^{a,†} Gaoran Li,^{a,†} Wenyao Zhang,^a Fei Lu,^{a,b} Dan Luo,^a Wenwen Liu,^a Aiping Yu,^{a,*} and Zhongwei Chena,^{*}

^aDepartment of Chemical Engineering, Waterloo Institute for Nanotechnology, University of Waterloo, Waterloo, Ontario N2L3G1, Canada.

^bCollege of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, P. R. China

Email: aipingyu@uwaterloo.ca (A. Yu); zhwchen@uwaterloo.ca (Z. Chen)

† These authors contribute equally to this work.

Experimental section

Synthesis of ZnHMT microflowers: The ZnHMT microflowers were prepared through a facile and fast solution-based process. Typically, 1.06 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.25 g HMT were dissolved in 15 mL and 12.5 mL anhydrous ethanol separately. After that, the $\text{Zn}(\text{NO}_3)_2$ solution was poured into the HMT solution, upon which the white precipitate can be immediately perceived. The mixture solution was then rest for an hour for complete reaction. Subsequently, the white precipitation was collected through vacuum filtration, washed with ethanol, and further dried at 80°C for 12 hrs. Additionally, the impacts of various synthesis parameters, including reactants molar ratio (Zn: HMT=1:1, 2:1, 4:1), reaction temperature (0, 20, 25, 30, 45 °C), reaction time (5 min, 30 min, 1 hr, 12 hrs) and water content in solvent (0, 1 and 10% in volume ratio), were also systematically investigated.

Fabrication of ZnHMT@PP separators: The ZnHMT@PP separator was prepared by simply casting the slurry containing the ZnHMT/SP mixture and polyvinylidene fluoride (PVDF) in weight ratio of 9:1 in 1-methyl-2-pyrrolidinone (NMP) solvent onto the conventional polypropylene-based membrane, and dried at 60 °C overnight. The areal mass loading of coating layer was controlled at 0.5 mg cm⁻². For comparison, ZnHMT@PP separators with varied ZnHMT to SP mass ratios of 2:1, 1:1 and 1:2 were also fabricated.

Preparation of S@SP cathode: The S@SP composite was firstly prepared through the traditional melt-diffusion method. Sulfur and super P powder was grinded in mass ratio of 7:3 followed by annealing at 155 °C for 6 hrs under argon atmosphere. After that, the S@SP electrodes were prepared by casting the homogeneous slurry containing S@SP composite, SP and PVDF in mass ratio of 8:1:1 in NMP solvent on aluminum foil and further dried at 60 °C overnight. The areal sulfur loading for regular electrodes was controlled at around 1.2 mg cm⁻², while higher sulfur loading of 4.5 mg cm⁻² was also prepared for higher energy density.

Characterization: The SEM (LEO 1530) and TEM (JEOL 2010F) images were performed to study the morphology and microstructures of the obtained materials. AFM (Bruker Innova) characterizations were conducted to determine the thickness of the obtained MOF nanosheets. XRD patterns were collected by MiniFlex 600 Rigaku diffractometer. FTIR spectra were collected by Thermo Nicolet Avatar 320. The surface

chemical states were analyzed by XPS using a Thermo Scientific K-Alpha XPS spectrometer. UV-vis tests were carried out on a Thermo Scientific GENESYS 10S spectrophotometer. The sulfur content was determined by TGA (TA instruments Q500) at a heating rate of 5 °C min⁻¹ under nitrogen atmosphere. The pore structures were measured by nitrogen sorption (ASAP 2020 micromeritics) and analyzed based on Brunauer-Emmett-Teller theory.

Electrochemical characterizations: CR2016-type coin cells were assembled by using the as-prepared S@SP composite electrode as cathode, lithium foil as anode, and different membranes (PP or ZnHMT@PP) as separator. The electrolyte contains 1M bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) in a mixture solvent of dimethoxymethane (DME) and 1,3-dioxolane (DOL) (1:1 in volume ratio) with 2 % lithium nitrate as additive. The electrolyte usage conforms an E/S ratio of 15 $\mu\text{L mg}^{-1}$. Galvanostatic cycling was conducted on LAND battery tester to evaluate the electrochemical performance. The current densities and capacities were calculated based on the mass of sulfur. CV curves were collected by Gamry 5000E workstation within the voltage range of 1.8-2.6 V (vs. Li⁺/Li) at a scanning rate of 0.1 mV s⁻¹. The EIS measurements were also performed by Gamry 5000E workstation in frequency range of 0.1 Hz to 100 kHz with an amplitude of 5 mV.

Supporting Figures

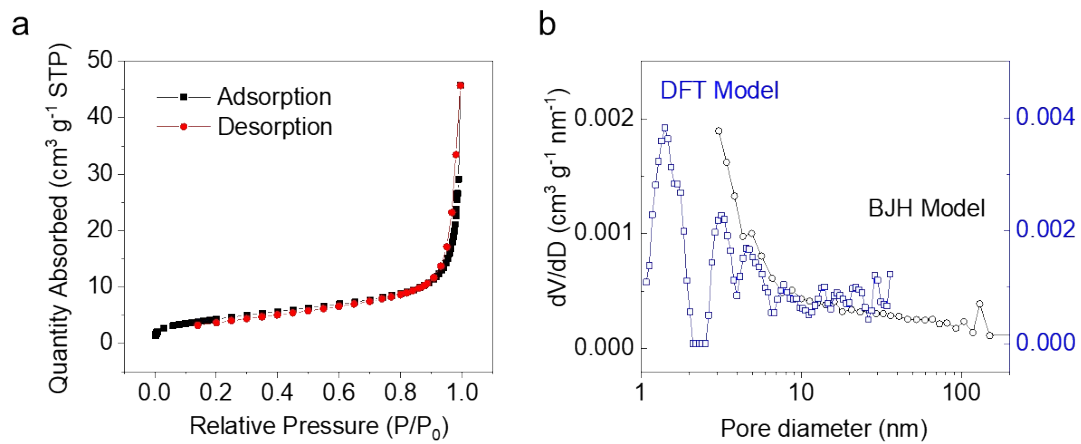


Fig. S1. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of ZnHMT microflowers.

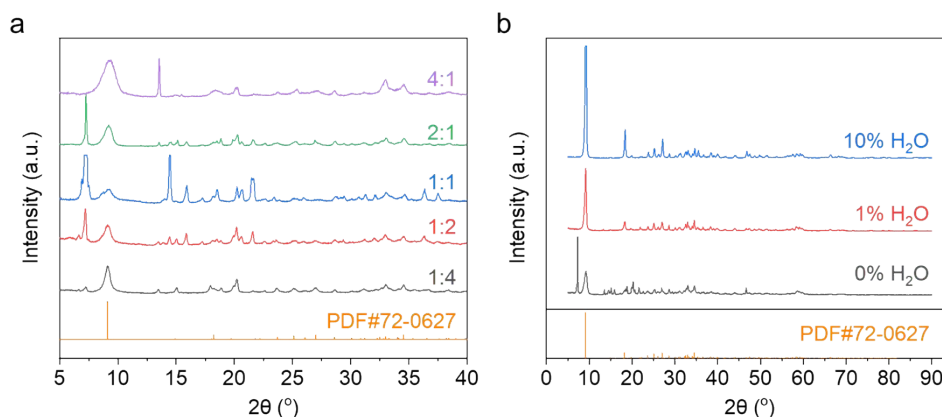


Fig. S2. XRD patterns of ZnHMT prepared under (a) different Zn to HMT ratios and (b) different H₂O contents in the solvent.

The XRD patterns in Fig. S2a reveal the existence of $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$ phase in the product, which can be ascribed to the partial hydrolysis of HMT triggered by the crystal water in zinc nitrate. The significant peak intensification with the increase of H₂O in Fig S2b also confirms the participation of HMT hydrolysis upon the synthesis. On the other hand, the strong C-N responses in XPS and FTIR spectra (Fig. 2b-e) verify the incorporation of HMT in the product. However, the rest peaks in XRD patterns cannot be well identified, thus the product is speculated as a mixture. The exact molecular/crystalline structure of ZnHMT is still vague and requires further investigation.

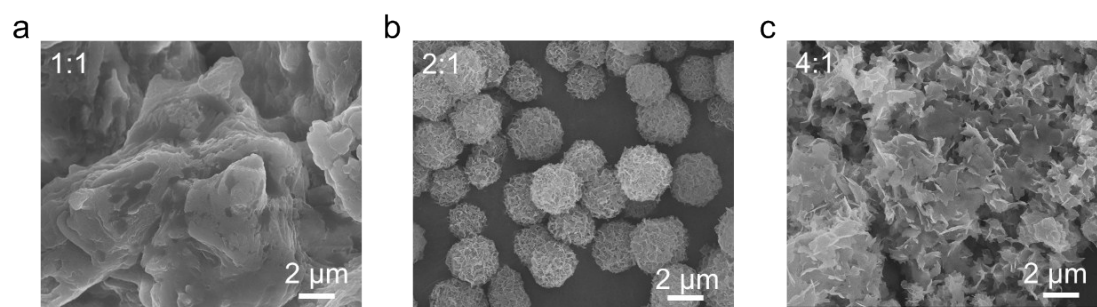


Fig. S3. SEM images of ZnHMT obtained at varied Zn(NO₃)₂ to HMT ratios.

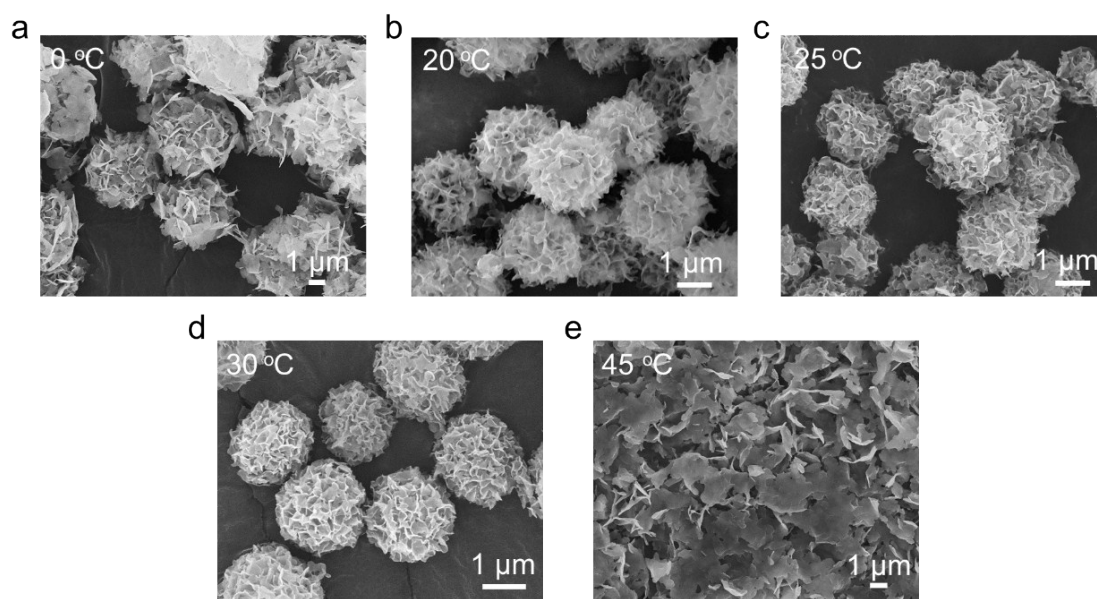


Fig. S4. SEM images of ZnHMT obtained at different temperatures.

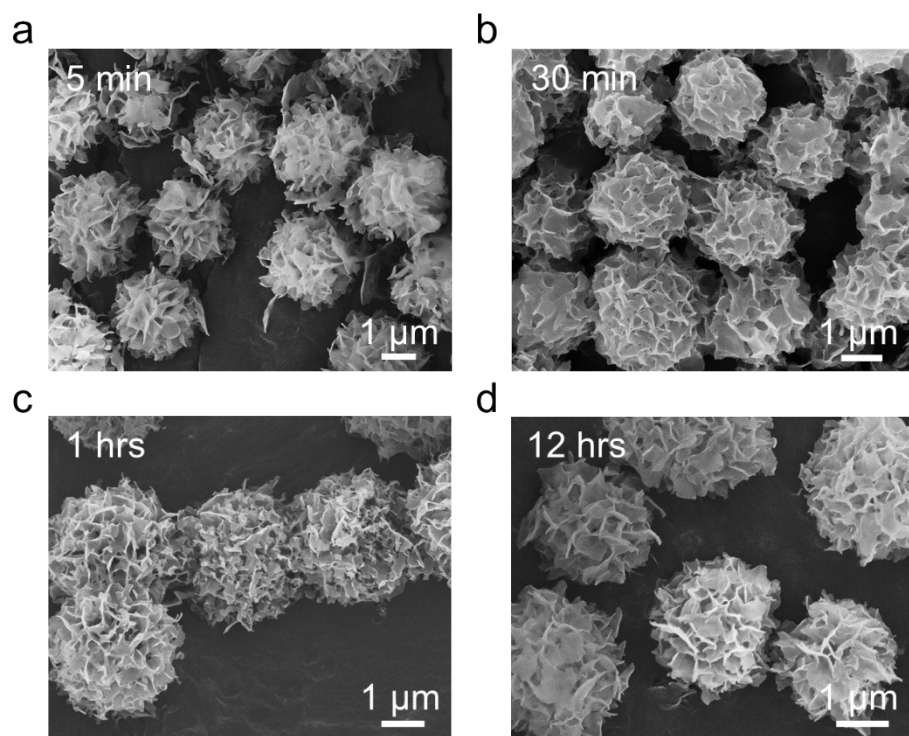


Fig. S5. SEM images of ZnHMT under different reaction time.

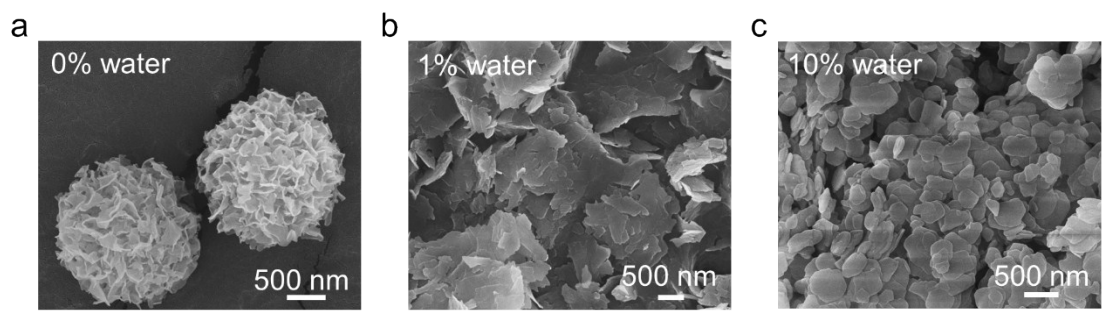


Fig. S6. SEM images of ZnHMT obtained under different water contents in solvent.

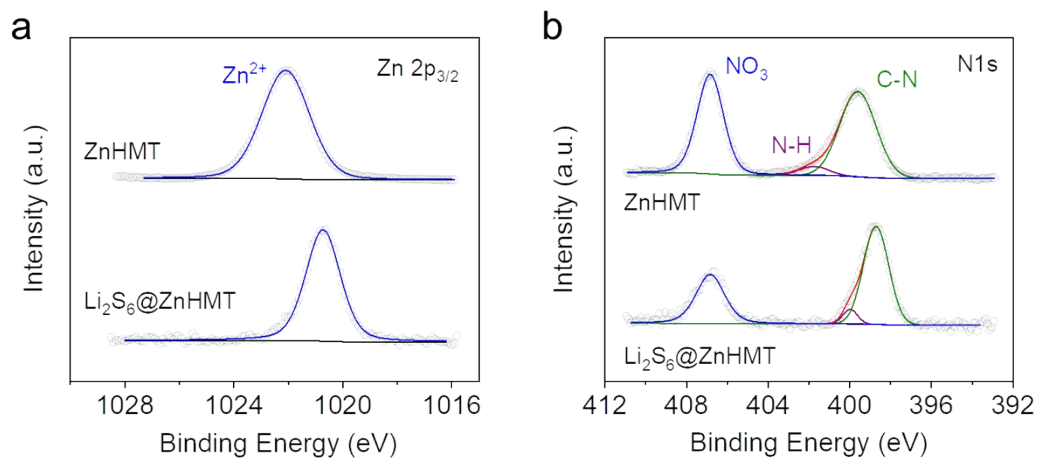


Fig. S7. (a) Zn $2p_{3/2}$ and (b) N 1s XPS spectra of ZnHMT and $\text{Li}_2\text{S}_6@\text{ZnHMT}$ composite.

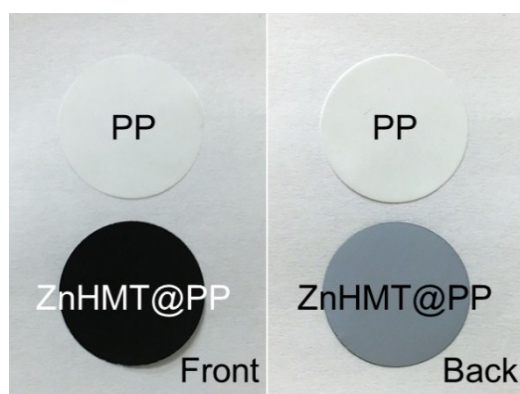


Fig. S8. (a) Optical images of PP and ZnHMT@PP separators at front and back side.

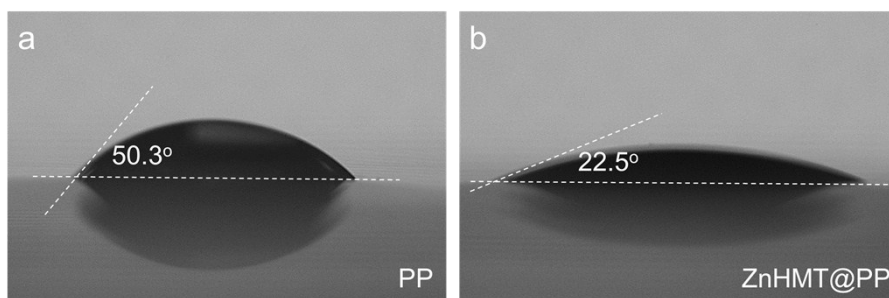


Fig. S9. Contact angles of electrolyte drop on (a) pristine PP and (b) ZnHMT@PP membranes.

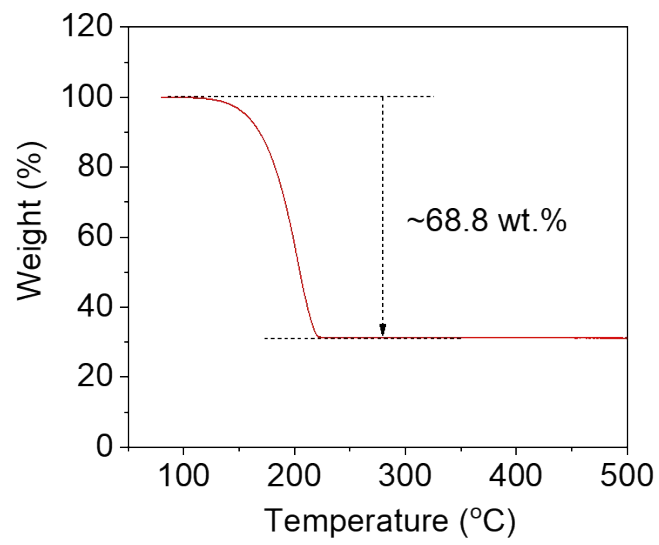


Fig. S10. TGA curve of S@SP composite.

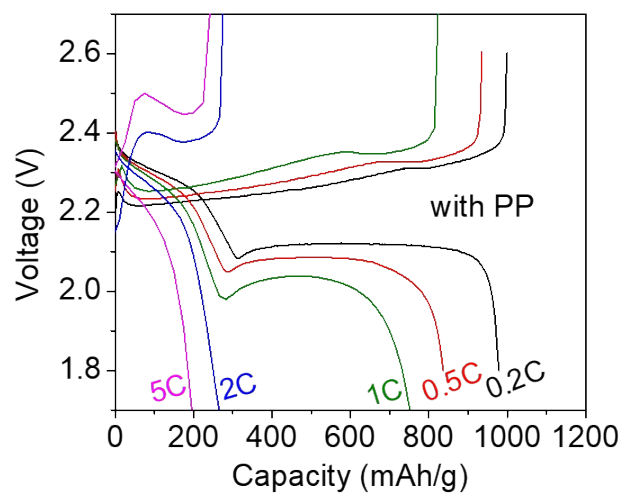


Fig. S11. Charge-discharge profile of PP cell at different current rates.

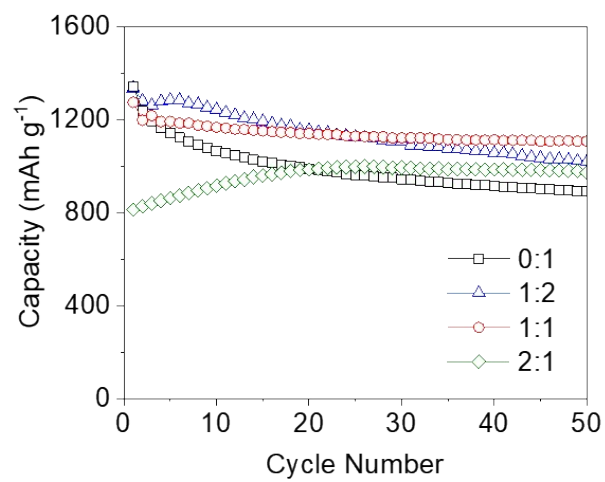


Fig. S12. Cycling performances of ZnHMT@PP cells at 0.2 C with different ZnHMT to SP ratios.

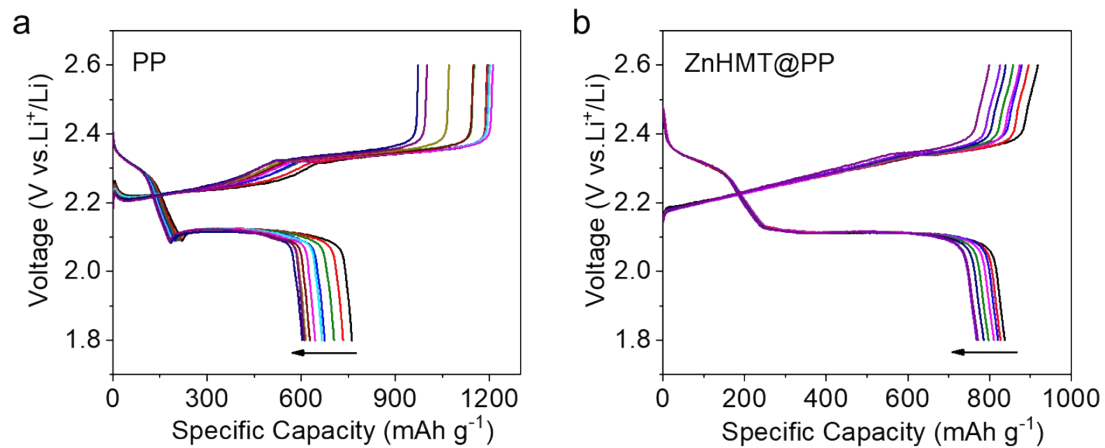


Fig. S13. Typical voltage profiles of (a) PP and (b) ZnHMT@PP cells at 0.2 C without LiNO₃ additive.

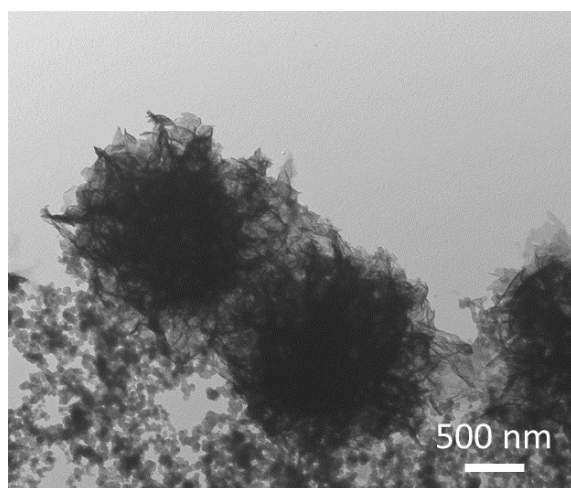


Fig. S14. TEM image of ZnHMT after cycling.

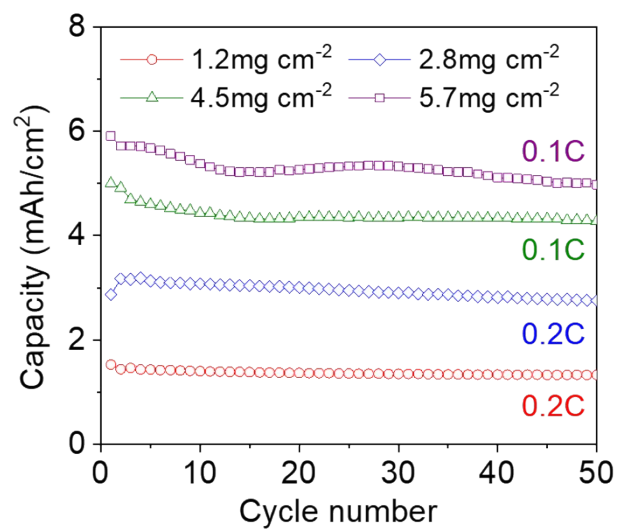


Fig. S15. Cycling performance of ZnHMT@PP cells under varied sulfur loadings.