Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Engineering a high-entropy oxide with high-density grain boundaries and strong *d-p* orbital coupling for advanced lithium-sulfur batteries

Chulong Liu,[a] *Rongjun Xie,*[a] *Jinrui Zhou,*[a] *Wenchang Xie,*[a] *Qidi Chen,*[a] *Daoping Cai,**[a] *Chaoqi Zhang,*[a] *and Hongbing Zhan**[ab]

[a] College of Materials Science and Engineering, Fuzhou University,
Fujian 350108, China.

[b] Fujian Science & Technological Innovation Lab Optoelect Informa,
Fuzhou 350108, China.

*Corresponding author: Daoping Cai and Hongbing Zhan.

E–mail address: dpcai@fzu.edu.cn; hbzhan@fzu.edu.cn.

Experimental section

1.1. Synthesis of HEO BiSbWVMoO

Firstly, 0.102 g of $Bi(NO_3)_3·5H_2O$, 0.048 g of $SbCl_3$, 0.500 g of polyvinylpyrrolidone (PVP, K30) and 25 mL of ethylene glycol were thoroughly mixed in the 50 mL beaker under ultrasonic dispersion to get a clear solution, denoted as solution A. Subsequently, 0.016 g of NH_4VO_3, 0.033 g of $Na_2MoO_4·2H_2O$, 0.046 g of $Na_2WO_4·2H_2O$ and 15 mL of deionized water were mixed in the 50 mL beaker under ultrasonic dispersion to get a clear solution, denoted as solution B. Thereafter, the solution B was slowly dropped into solution A with stirring to form a Pale solution and stirring for 10 min. The resulting solution was transferred into a 50 mL Teflon-lined autoclave with a stainless-steel shell and kept at 150 °C for 10 h. After cooling naturally, the obtained sample was collected by centrifugation and washed with ethanol and deionized water several times and finally dried overnight in air.

1.2. Synthesis of Bi_2WO_6

Typically, 0.205 g of $Bi(NO_3)_3·5H_2O$, 0.500 g of PVP and 25 mL of ethylene glycol were thoroughly mixed in the 50 mL beaker under ultrasonic dispersion to get a clear solution, denoted as solution A. Then, 0.07 g of $Na_2WO_4·2H_2O$ and 15 mL of deionized water were mixed in the 50 mL beaker under ultrasonic dispersion to get a clear solution, denoted as solution B. After that, the solution B was slowly dropped into the solution A with stirring to form a Pale yellow solution and stirring for 10 min. The resulting solution was transferred into a 50 mL Teflon-lined autoclave with a stainless-steel shell and kept at 150 °C for 10 h. After cooling naturally, the obtained sample was collected by centrifugation and washed with ethanol and deionized water several times and finally dried overnight in air.

1.3. Synthesis of KB/S

Fabrication of sulfur cathode: the sublimed sulfur (75%) and ketjen black (KB) (25%) were fully ground and sealed in a sealed glass bottle. Then, it was placed in the quartz tube and heated at 155 °C for 12 hours. Afterward, KB/S, KB, polyvinylidene fluoride (PVDF) were sufficiently mixed with a ratio of 8:1:1 and evenly dispersed into 1-methyl-2-pyrrolidinone (NMP) to form a uniform slurry, which was coated on carbon-coated Al foil and dried in a vacuum oven at 60 °C for 4 h. The mass loading of sulfur was around 1.0-1.5 mg cm^{-2}.

1.4. Preparation of the modified separator

The HEO BiSbWVMoO layer uniformly coated on Celgard 2500 polypropylene (PP) separator was obtained by the vacuum filtration method. 70 wt% of HEO BiSbWVMoO, 20 wt% of PVDF and 10 wt% of Super P were dispersed in NMP solvent by sonication for 2 h to obtain a homogeneous suspension, which was filtered through the PP separator (Celgard 2500). The obtained functionalized separator was dried at 70 °C overnight. Eventually, the modified separator was cut into discs with a diameter of 19 mm. The Bi_2WO_6 functional separator was prepared using the same method. The functional separator possessed a thickness of about 4.9 μm and the areal mass loading of the coating layer materials was controlled at about 0.45 mg cm^{-2}.

1.5. Lithium polysulfide (Li_2S_6) solution and visualized adsorption test

The Li_2S_6 solution was prepared by adding Li_2S (0.115 g) and S (0.4 g) with a mass ratio of 1:5 in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 in volume) under vigorous stirring at 70 °C for 24 h. After that, 20 mg of HEO BiSbWVMoO and Bi_2WO_6 samples were respectively added into 3 mL solution (5 mM) for visualized adsorption test. All the above operations were carried out in an argon-filled glove box.

1.6. Li_2S_6 symmetric cell assembly and kinetic evaluation of polysulfides conversion

The CR2032-coin cells were assembled using PP separator between two symmetric electrodes containing HEO BiSbWVMoO or Bi_2WO_6. Similarly, reference symmetric cell without Li_2S_6 was assembled by the same way. The electrolyte was 0.25 M Li_2S_6 in 1,3-dioxolane (DOL) and dimethyl ether (DME) (v/v = 1:1) with 1.0 wt% $LiNO_3$ as electrolyte. The amount of liquid electrolyte in each coin cell was about 40 μL. The cyclic voltammetry (CV) curves of symmetric batteries were investigated to evaluate LiPSs redox kinetics at voltage range from -1.0 to 1.0 V with scanning rate of 5 mV s^{-1}.

1.7. Li_2S nucleation and decomposition measurements

For the study of liquid-solid conversion kinetics, Li_2S_8 solution (0.5 M) was prepared by mixing sulfur and lithium sulfide (molar ratio of 7:1) and dissolving the mixture in DME and DOL (1:1 in volume) solution containing 1.0 M LiTFSI under vigorous stirring for 24 h. Precipitation of Li_2S on various reactive surfaces was investigated in 2032 coin-type cells with a Celgard 2500 PP separator. 20 μL of 0.5 M Li_2S_8 was dropped on the cathode, and 20 μL of LiTFSI electrolyte was used on the anode. The cells were discharged galvanostatically at 0.1 mA to 2.19 V, and then kept at 2.12 V for Li_2S to nucleate until the current dropped below 10^{-5} A. For the measurement of Li_2S dissolution, the coin cells were galvanostatically discharged at 0.112 mA to 1.70 V and then potentiostatically charged at 2.4 V for the adequate dissolution of Li_2S.

2.1. Materials characterization

The information of composition, microstructure and morphology of the products were analyzed by X-ray diffractometer (XRD, Rigaku, D/max-UItima III difractometer, Cu Kα radiation, $\lambda = 0.15418$ nm), X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250), field emission scanning electron microscope (FESEM, Germany, Zeiss Supra 55), high-resolution transmission electron microscope (HRTEM, FEI, Talos F200i), and the thermogravimetric analysis (TGA, NETZSCH, STA449-F5).

2.2. Electrochemical measurements

CR2032-type cells were assembled with KB/S cathode, the as-prepared modified separators, lithium metal anode, and an electrolyte of 1.0 M LiTFSI (1M in DOL/DME, volume ratio 1:1) with 1 wt% of $LiNO_3$. Galvanostatic charge and discharge (GCD) tests were conducted on Neware BTS4008 within a potential range from 1.7 to 2.8 V. The specific capacity was calculated based on the weight of sulfur in each cell (1 C = 1675 mA g^{-1}). CV curves and electrochemical impedance spectroscopy (EIS) were measured by an electrochemical workstation (CHI660E). EIS profiles were tested with the frequency range from 10^{-2} to 10^{5} Hz.

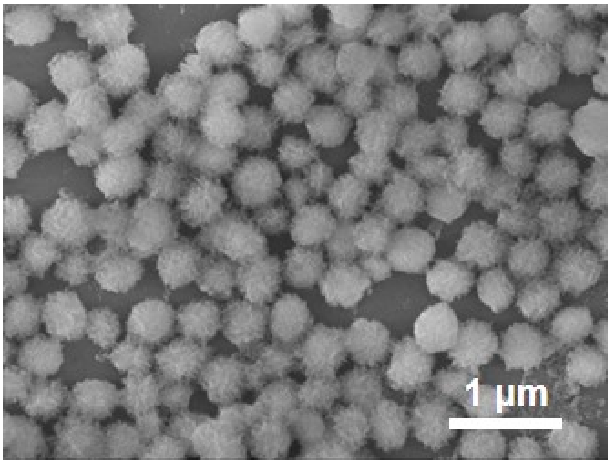


Fig S1. SEM image of the HEO BiSbWVMoO.

Fig S2. EDS spectrum of the HEO BiSbWVMoO.

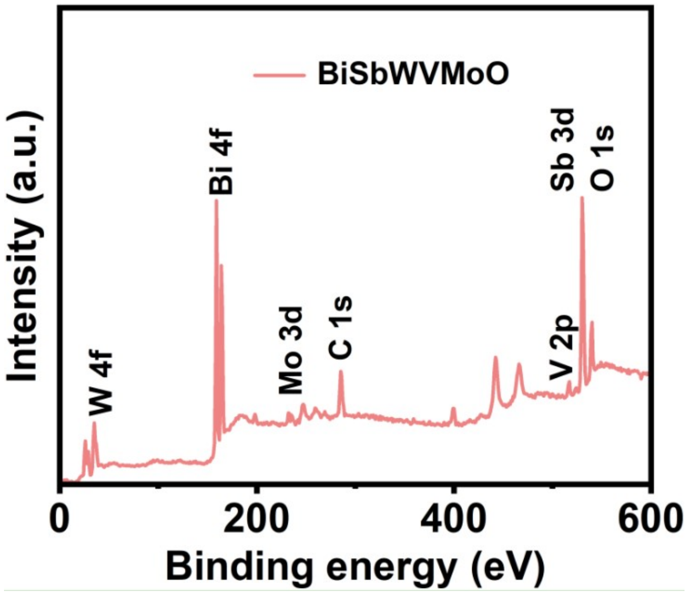


Fig. S3. XPS survey spectrum of the HEO BiSbWVMoO.

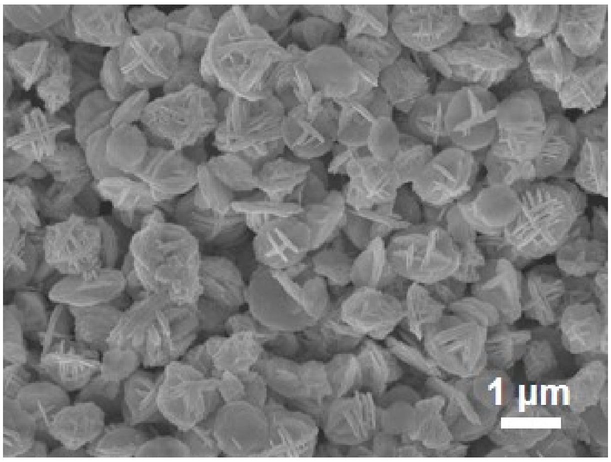
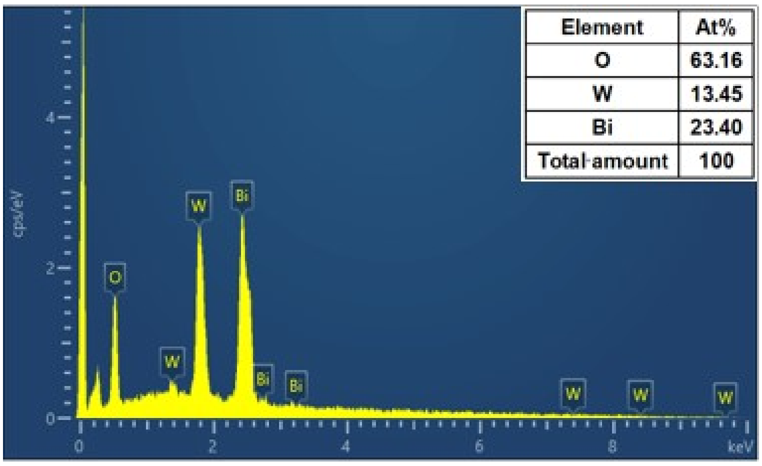


Fig S4. SEM image of the Bi_2WO_6 counterpart.



Element	At%
O	63.16
W	13.45
Bi	23.40
Total amount	100

Fig S5. EDS spectrum of the Bi_2WO_6.

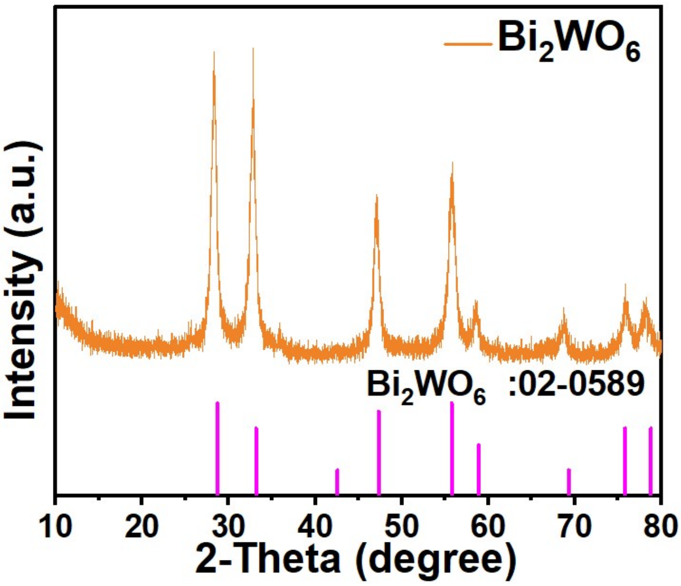


Fig S6. XRD pattern of the Bi_2WO_6.

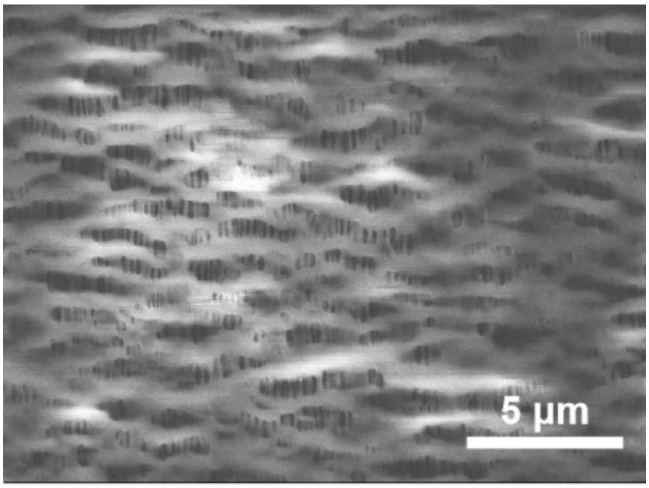


Fig S7. SEM image of the pristine PP separator.

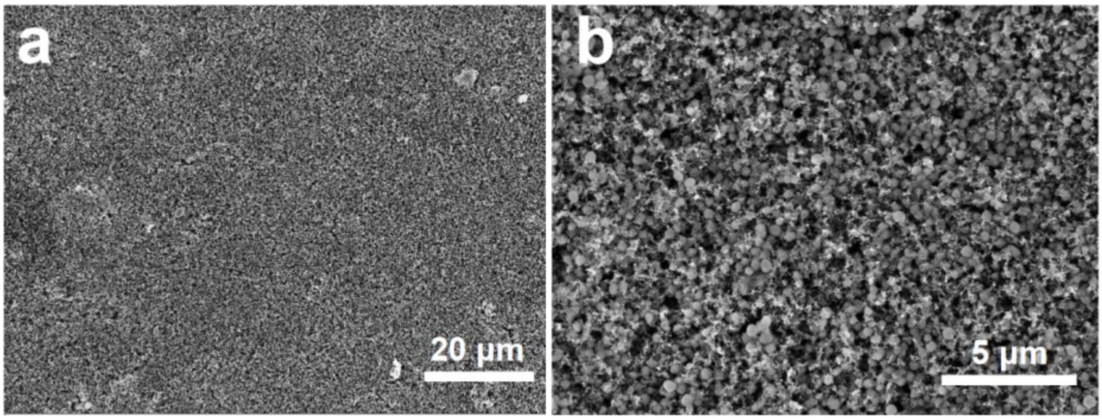


Fig S8. (a,b) SEM images of the HEO BiSbWVMoO coating layer (top-view).

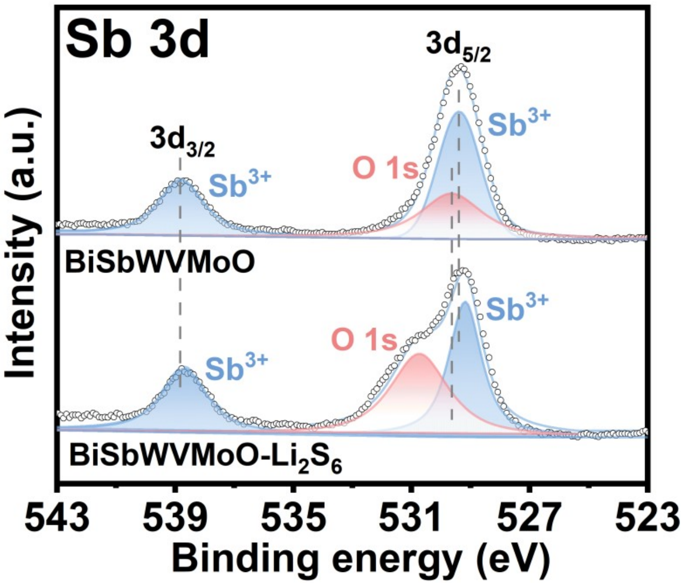


Fig. S9. High-resolution Sb 3d XPS spectrum of the HEO BiSbWVMoO after Li_2S_6 adsorption.

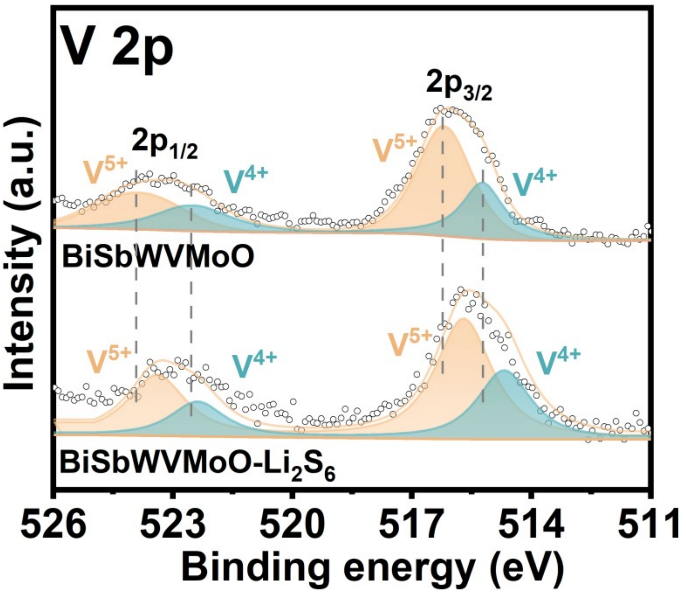


Fig. S10. High-resolution V 2p XPS spectrum of the HEO BiSbWVMoO after Li_2S_6 adsorption.

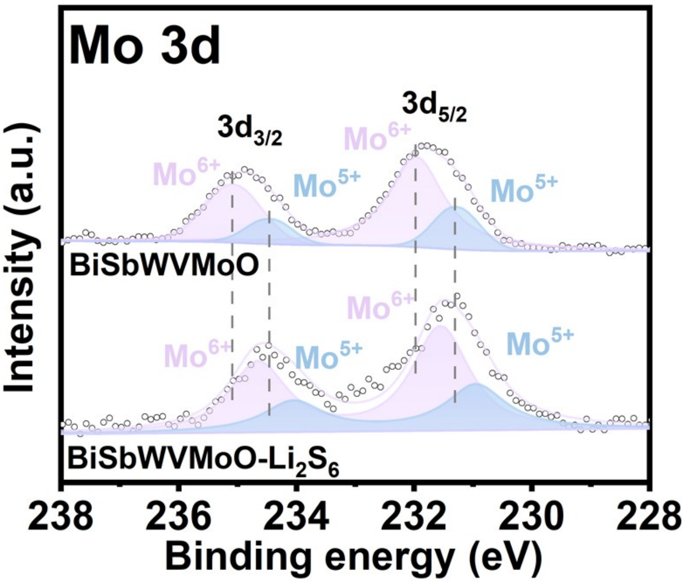


Fig. S11. High-resolution Mo 3d XPS spectrum of the HEO BiSbWVMoO after Li_2S_6 adsorption.

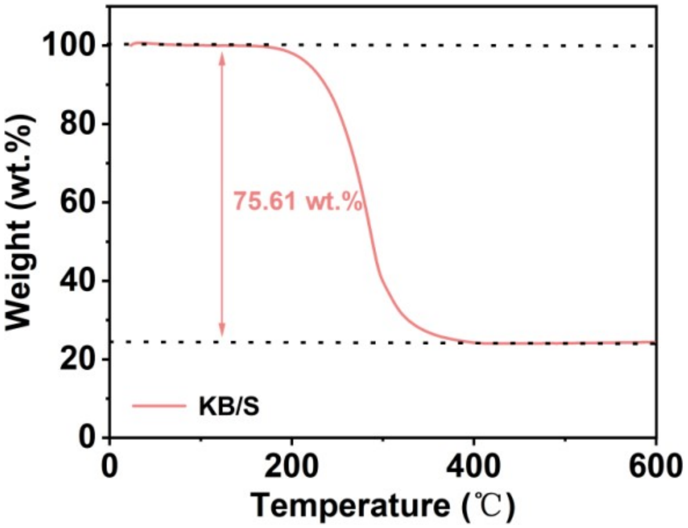


Fig. S12. TGA curve of the KB/S composite.

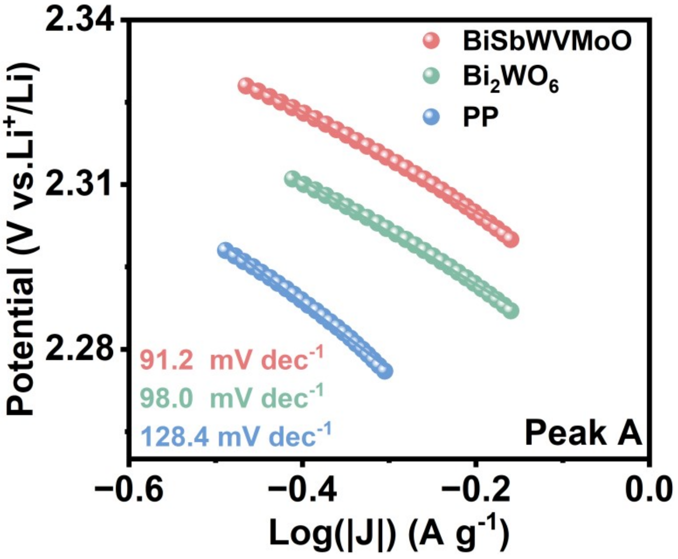


Fig. S13. The derived Tafel plots of Peak A for different Li-S batteries.

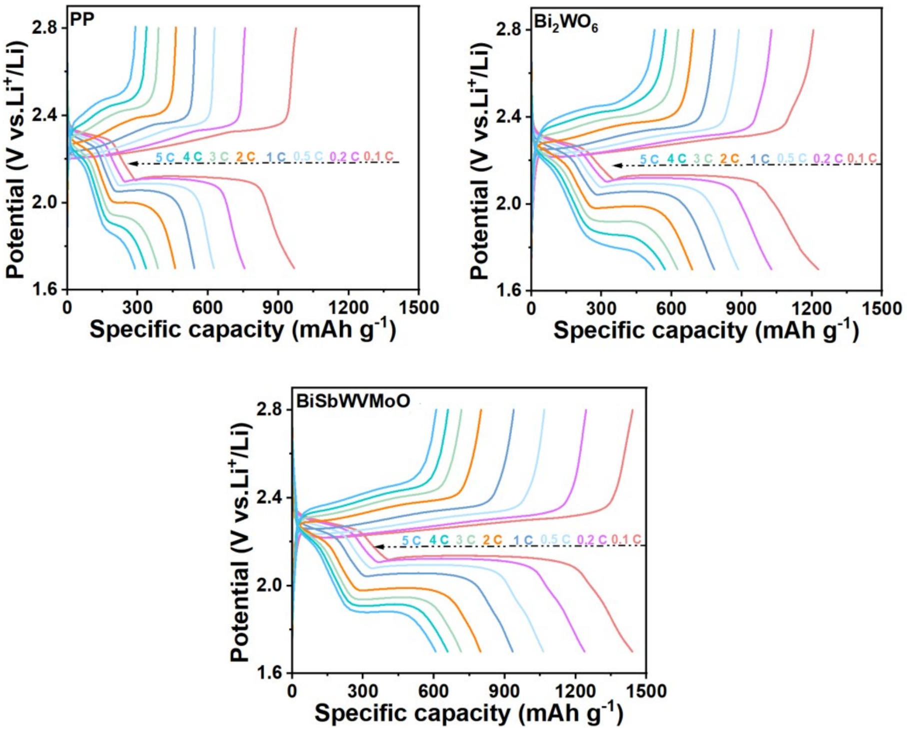


Fig. S14. GCD profiles of the Li-S batteries with (a) PP, (b) Bi_2WO_6 and (c) HEO BiSbWVMoO separators at various current densities.

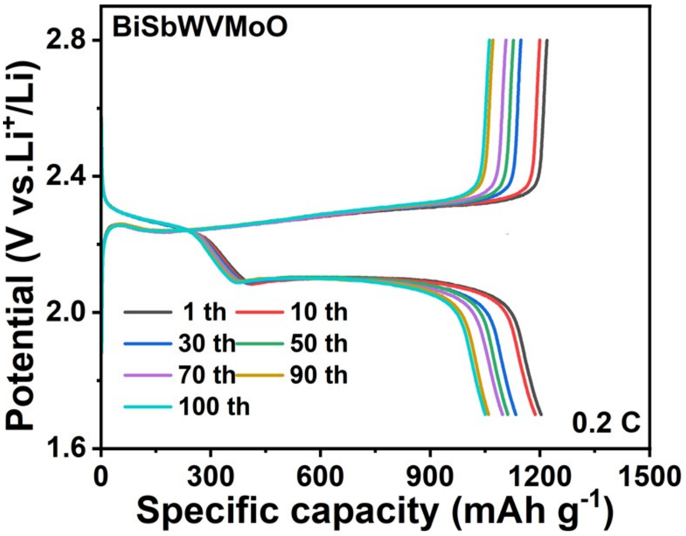


Fig. S15. GCD profiles of the Li-S battery with HEO BiSbWVMoO separator at 0.2 C.

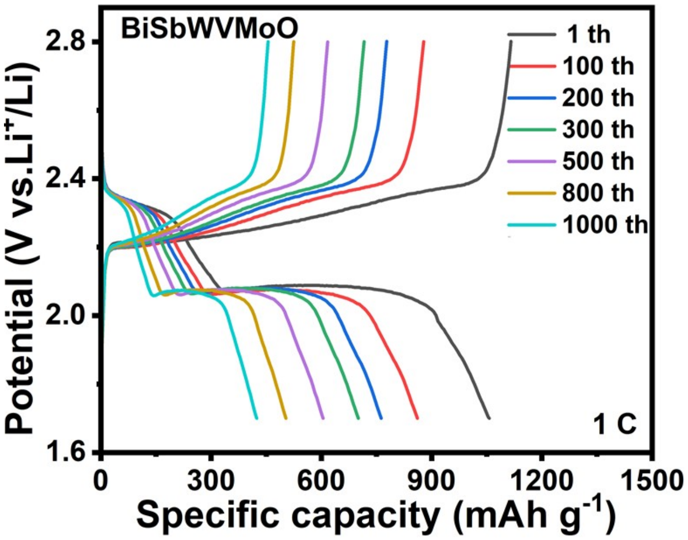


Fig. S16. GCD profiles of the Li-S battery with HEO BiSbWVMoO separator at 1 C.

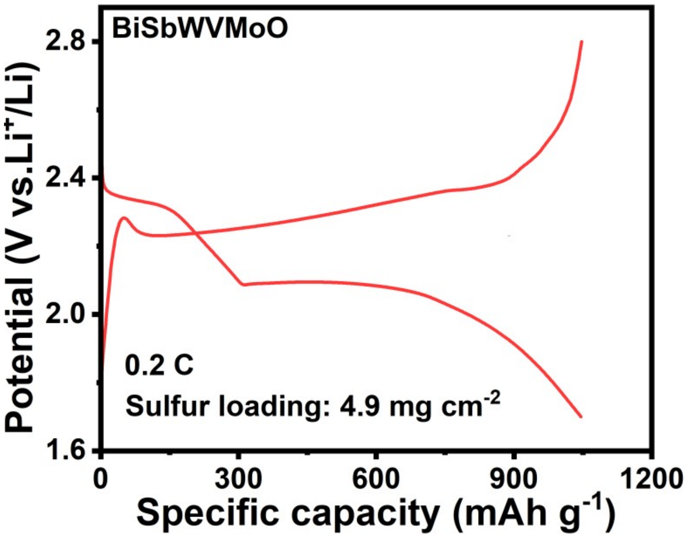


Fig. S17. The initial GCD profiles of the HEO BiSbWVMoO battery at 0.2 C.

Table S1. Lithium-ion diffusion rates (D_{Li+}, cm^2 s^{-1}) of the Li-S batteries with different separators.

Separators	Peak A (cm^2 s^{-1})	Peak B (cm^2 s^{-1})	Peak C (cm^2 s^{-1})
PP	1.02×10^{-8}	1.36×10^{-8}	4.83×10^{-8}
Bi_2WO_6	1.50×10^{-8}	1.86×10^{-8}	5.98×10^{-8}
HEO BiSbWVMoO	1.91×10^{-8}	2.70×10^{-8}	9.08×10^{-8}

Table S2. Comparison of the electrochemical performance of HEO BiSbWVMoO with other recently reported materials.

Catalytic materials	**Cycle performance (mAh g^{-1})**	**High rate (mAh g^{-1})**	**Long cycle stability (mAh g^{-1})**	**Capacity Decay rate (cycle^{-1})**	**References**
CoO/NiO@C-NC	920.0/100/0.2 C	738.0 (3 C)	665.0/500/1 C	0.075%	19
CoNiCuMnZnFe-PBA	570.9/200/0.1 C	424.0 (1 C)	424.9/200/0.5 C	0.201%	31
$(Mg_{0.2}Mn_{0.2}Ni_{0.2}Co_{0.2}Zn_{0.2})Fe_2O_4$	879.6/100/0.1 C	632.1 (5 C)	558.4/500/1 C	0.073%	33
$(Cu_{0.7}\,Fe_{0.6}Mn_{0.4}Ni_{0.6}Sn_{0.5})O_4$	~590.0/200/0.5 C	849.0 (2 C)	435.0/400/1 C	0.130%	35
NiMgCuZnCoO	664.0/200/0.1 C	634.0 (1 C)	479.0/600/0.5 C	0.077%	37
FeCoNiZnCu-NCNT	976.2/100/0.1 C	679.7 (2 C)	466.3/600/1 C	0.072%	41
CoFeMnO-YSNCs	~780/100/0.2 C	651.0 (3 C)	609.3/600/1 C	0.060%	54
CNT/CoNiFeCu-NC	820.2/100/0.2 C	521.1 (5 C)	692.0/300/1 C	0.058%	55
$NiCoCuTiVS_x$	968.9/200/0.5 C	560.2 (2 C)	725.4/230/1 C	0.154%	57
$CoN\text{-}Mo_2N$	866.9/200/0.2 C	613.9 (2 C)	549.5/500/1 C	0.107%	58
CoNi@mG	~630.0/100/0.2 C	528.6 (3 C)	~380.0/1000/1 C	0.055%	59
$(CrMnFeNiMg)_3O_4$	817.0/100/0.1 C	373.0 (1 C)	421.2/200/1 C	0.140%	60
$a\text{-}TiO_2/a\text{-}MoS_2$	726.0/200/0.5 C	549.0 (3 C)	513.0/500/2 C	0.100%	61
$(Ni_{0.2}Co_{0.2}Mn_{0.2}Cu_{0.2}Zn_{0.2})WO_4$	~812.1/100/0.1 C	656.3 (5 C)	516.0/500/1 C	0.080%	62
HEO BiSbWVMoO	1053.2/100/0.2 C	607.9 (5 C)	504.0/1000/1 C	0.053%	This work

Table S3. Comparison of the electrochemical performance at high sulfur loading of this work with recently reported Li-S batteries.

Catalytic materials	**Sulfur loading (mg cm^{-2})**	**E/S ratio (μL mg^{-1})**	**Areal capacity (mAh cm^{-2})**	**Specific capacity (mAh mg^{-1})**	**References**
$(Mg_{0.2}Mn_{0.2}Ni_{0.2}Co_{0.2}Zn_{0.2})Fe_2O_4$	4.6	15.0	4.4/0.1 C	956.5	33
CoNiFePdV HEA	4.5	5.0	3.2/0.1 C	~710.0	34
$(Cu_{0.7}Fe_{0.6}Mn_{0.4}Ni_{0.6}Sn_{0.5})O_4$	3.4	/	2.8/0.2 C	824.0	35
$(Ni_{0.2}Co_{0.2}Cu_{0.2}Mg_{0.2}Zn_{0.2})O$	4.4	5.0	3.7/0.1 C	850.0	39
FeCoNiZnCu-NCNT	4.5	/	2.8/0.1 C	637.4	41
CoFeMnO-YSNCs	4.3	7.4	4.5/0.1 C	~1046.5	54
CNT/CoNiFeCu-NC	4.2	/	4.2/0.1 C	803.8	55
$Ni_3V_2O_8$@CNTs	2.5	7.8	2.2/0.1 C	~880.0	56
CoNi@mG	4.9	5.6	4.2/0.1 C	857.1	59
a-TiO_2/a-MoS_2	4.7	12.0	3.6/0.1 C	772.0	61
HEO BiSbWVMoO	4.9	8.2	5.1/0.2 C	1046.0	This work