Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

A Multifunctional Separator Modified by Y_2O_3/Co_3O_4 Heterostructures Boosting Polysulfides Catalytic Conversion for Advanced Li-S Batteries

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1.Experimental Section

1.1 Synthesis of Y_2O_3/Co_3O_4/AB and Co_3O_4/AB composite

Cobalt acetate tetrahydrate (II) and yttrium nitrate hexahydrate （III） were purchased from Aladdin Reagent Co., LTD. (Shanghai, China), and acetylene black was obtained

from Power Source Battery Material Co., LTD. (Shanxi, China).

Y_2O_3/Co_3O_4/AB composite was made by a simple one-pot process. 1 g cobalt acetate tetrahydrate (II), 0.255 g yttrium nitrate hexahydrate (III) and 3 g urea were added into 80 ml deionized water. After that, the prepared solution was stirred magnetically for 1 h to mix and dissolve and then transferred to a 100 ml teflon reactor at 180 ^{o}C for 12 h. Then, the reactant solution was washed with deionized water and anhydrous ethanol and pumped to collect the precipitate. Afterwards, the precipitate was calcined in a tube furnace at 800 ^{o}C under an air atmosphere for 2 h to obtain the Y_2O_3/Co_3O_4 composite. Next, the obtained composite and acetylene black were added into anhydrous ethanol in a ratio of 4:6 for ultrasonic dispersion and stirring for 2 h. Finally, the Y_2O_3/Co_3O_4/AB composite was obtained by filtration and drying at 60 ^{o}C for 10 h.

The synthesis process of Co_3O_4/AB composite was basically same as Y_2O_3/Co_3O_4/AB composite except that yttrium nitrate hexahydrate (III) was not added at the beginning.

1.2 Material characterizations

The morphology and microstructure of Y_2O_3/Co_3O_4/AB were measured by scanning electron microscope (SEM,) and transmission electron microscope (TEM, FEI Talos F200X, UAS). The crystal pattern of Y_2O_3/Co_3O_4/AB and Co_3O_4/AB was gauged by X-ray diffraction (XRD, Rigaku Ultima IV) at 10-80° with the help of Cu Kα radiation. The specific surface area and pore size of Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB were tested by Brunauer-Emmett-Teller method (BET, ASAP 2460). The AB content in the Y_2O_3/Co_3O_4/AB and Co_3O_4/AB composite were obtained by thermogravimetric analysis (TGA, NETZSCH TG 209 F3). The chemical states of Y_2O_3/Co_3O_4/AB were carried out by X-ray photoelectron spectroscopy (XPS, AXIS SUPRA).

1.3 Preparation of Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB modified separator

The modified separator was prepared by simple coating method. 80 wt% Y_2O_3/Co_3O_4/AB composite and 20 wt% poly(vinylidene difluoride)(PVDF) were mixed uniformly in N-methy pyrrolidinone (NMP) .Then the slurry was coated onto the one side of blank Celgard 2400 separator. Next, the separator withY_2O_3/Co_3O_4/AB composite was dried in an oven at 60 ^oC for 12 h. Finally, the Y_2O_3/Co_3O_4/AB modified separator was cut into wafers with a diameter of 19 mm to assemble coin cell. The fabrication of Co_3O_4/AB and AB modified separator was similar with the above. The separator loading containing material is approximately 0.26 mg cm^{-2}.

1.4 Preparation of sulfur cathode

First of all, 70 wt% powdered sulfur, 20 wt% AB and 10 wt% PVDF were mixed uniformly in NMP and stirring for 12 h under room temperature. Then the slurry was coated onto the one side of aluminum foil and then dried in oven at 60 ^oC for 12 h. Finally, the obtained cathode was cut into wafers with a diameter of 8 mm to assemble coin cell. The sulfur cathode loading is approximately 1-7 mg cm^{-2}.

1.5 Visual absorption measurement

Firstly, S and Li_2S were mixed up into the isometric DOL and DME with a molar ration of 5:1 to obtain 1.5 mM Li_2S_6 solution. Then, the Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB composite with the same specific surface area were weighed and added to the same volume of 1.5 mM Li_2S_6 solution. Finally, the supernatant solution was extracted to carry out UV-Visible spectrum after 24h.

1.6 Symmetric cell experiment

80 wt% Y_2O_3/Co_3O_4/AB (Co_3O_4/AB or AB) and 20 wt% PVDF were dissolved into NMP to obtained a uniform slurry. Then the slurry was coated onto the aluminum foil. The foil was dried in an oven at 60 °C for 12 h and cut into wafers with a diameter of 8 mm. S and Li_2S were mixed with a molar ration of 5:1 into bis(trifluoromethanesulfonyl)imide lithium (LiTFSI) in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v=1:1) to obtain 0.5 M Li_2S_6 solution. The symmetric cell was assembled by identical cathode and anode which is the Y_2O_3/Co_3O_4/AB composite foil above with the electrolyte was 0.5 M Li_2S_6 solution above in an Ar-filled glove box. The cyclic voltage (CV) measurements were carried out at a scan rate of 10 mV/s from -0.6 V to 0.6 V.[1]

1.7 The nucleation and dissolution experiment of Li_2S

Li_2S nucleation measurement: S and Li_2S were dissolved with a molar ration of 5:1 in DME/DOL (v/v = 1/1) under stirring continuously for 24 h to obtain the 0.2 M Li_2S_8 solution. Then the slurry containing 90 wt% Y_2O_3/Co_3O_4/AB (Co_3O_4/AB or AB) and 10 wt% PVDF was dissolved into NMP was coated onto the carbon cloth. After 60 °C for 12 h in oven, the carbon cloth was cut into wafers with a diameter of 8 mm as the working electrode, and the lithium foil was used as the counter electrode with the blank Celgard 2400 separator. Notably, 20 μL 0.2 M Li_2S_8 solution as the catholyte was instilled on the cathode side, 20 μL DME/DOL (v/v = 1/1) solution as the anolyte was added on the anode side. Potentiistatic intermittent titration technique (PITT) measurements were gauged on a CHI660E electrochemical workstation. Firstly, the as-assembled cell was galvanostatically discharged at 0.112 mA until the voltage reduced to 2.06 V. Then the cell was potentiostatically discharged at 2.05 V until the current lessened to 10^{-5} A.

Li_2S dissolution measurement: The as-assembled cell was galvanostatically discharge at 0.112 mA until the potential decrease to 1.7 V. Then the cell was potentiostatically charged at 2.4 V until the current was reduced to 10^{-5} A.[2,3]

1.8 Electrochemical measurements

CR 2032 cells were assembled using the above cathode, the as-prepared modified separators (Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB) and the lithium metal foil as anode in an Ar-filled glove box (O_2, H_2O <0.01 ppm). The electrolyte made of 1 M LiTFSI dispersed in DOL/DME (v/v=1:1) with an additive of 0.1 M $LiNO_3$. The galvanostatic discharge/charge measurement was gauged by the Neware battery test system. The cyclic voltage (CV) measurements at the scanning rate of 0.1-1.0 mV s^{-1} in potential from 1.8 to 2.8 V (vs. Li/Li^+). The frequency range of electrochemical impedance spectroscopy (EIS) test was from 100 KHz to 0.01 Hz. The CV and EIS tests were analyzed by the CHI660E electrochemical workstation.

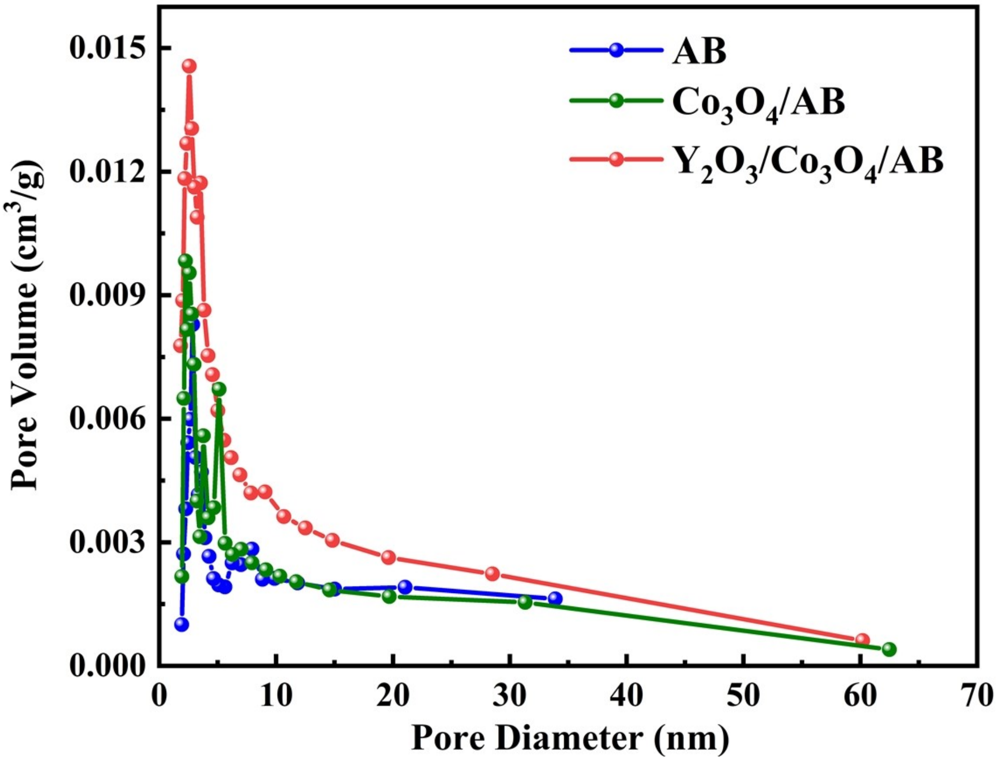

Figure.S1. Pore size distribution of Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB.

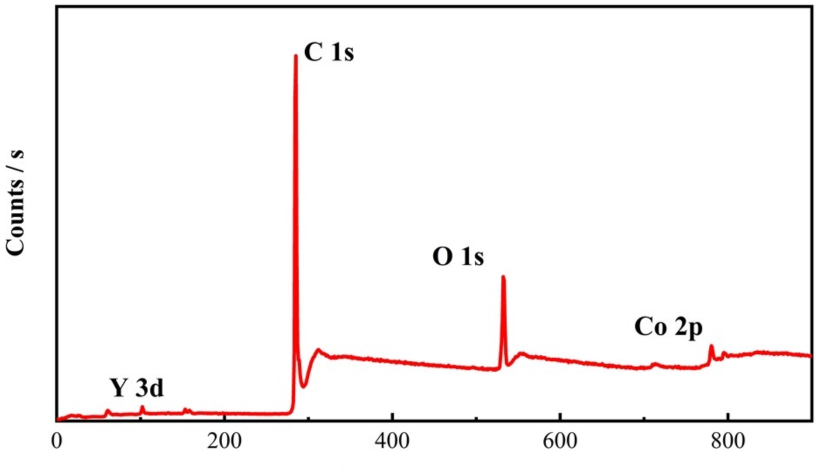

Figure.S2. XPS survey spectra of Y_2O_3/Co_3O_4/AB.

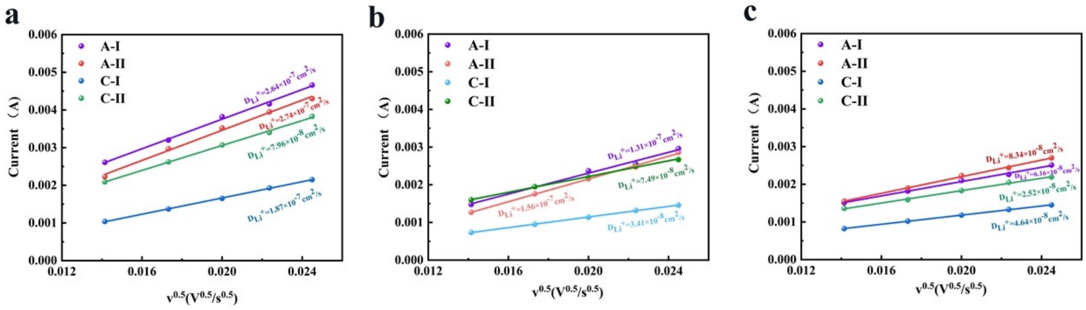

Figure.S3. Linear relationship between peak current I_p and the square root of scan rate $v^{0.5}$ of (a)$Y_2O_3/Co_3O_4/AB$, (b)Co_3O_4/AB and (c)AB.

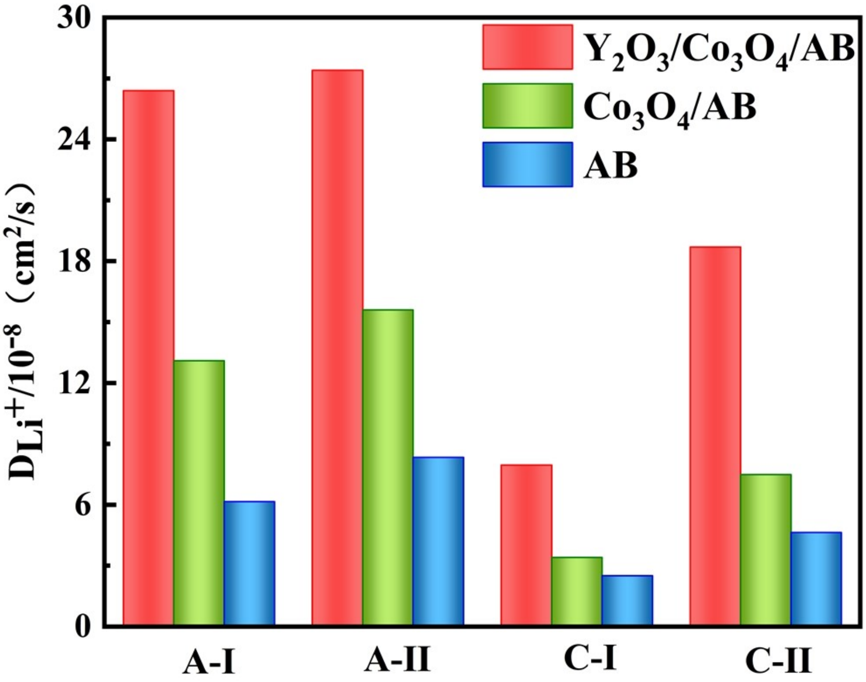

Figure.S4. Comparison of diffusion coefficients at different peak currents of $Y_2O_3/Co_3O_4/AB$, Co_3O_4/AB and AB.

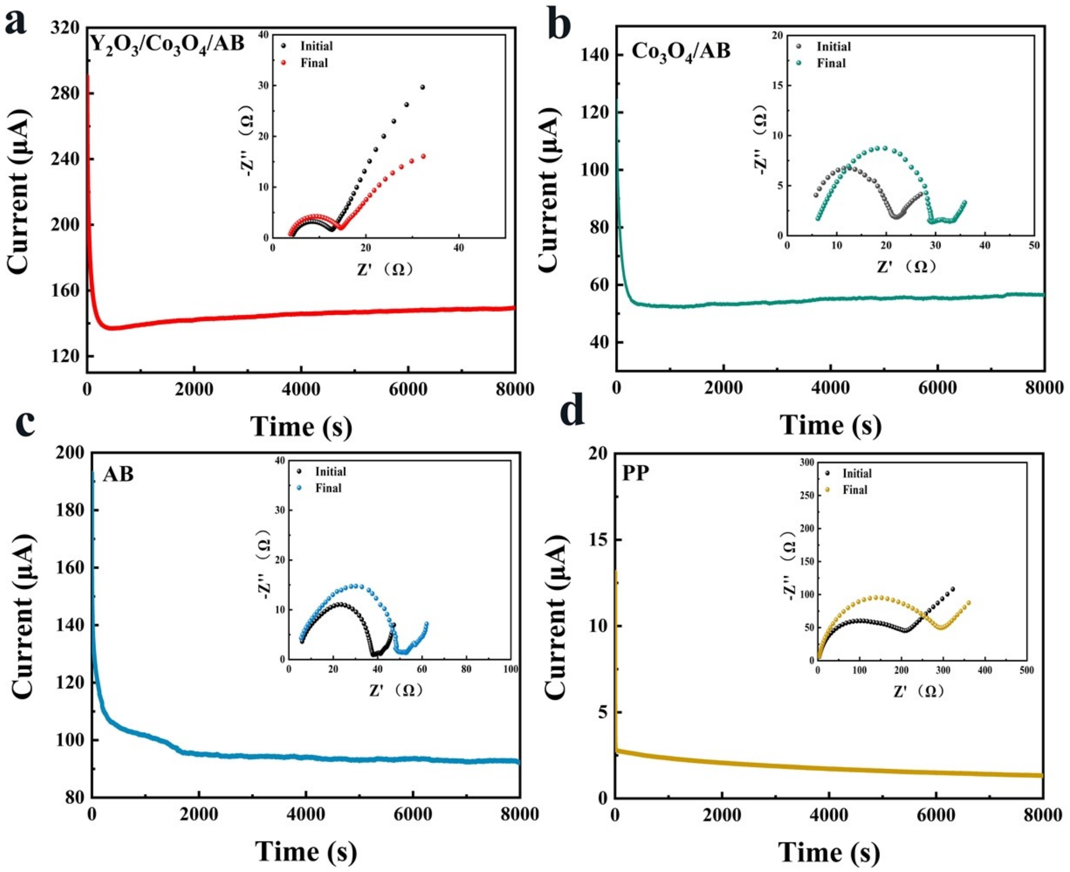

Figure.S5. t_{Li+} of (a)Y_2O_3/Co_3O_4/AB, (b)Co_3O_4/AB and (c)AB.

Table S1. t_{Li+} of Y_2O_3/Co_3O_4/AB, Co_3O_4/AB and AB

Separator	I_0/μA	I_s/μA	ΔV/ mV	R_0/Ω	R_s/Ω	t_{Li+}
PP	13	1.2	10	220	300	0.07
AB	193	93	10	41	53	0.20
Co_3O_4/AB	124	56	10	22	30	0.39
Y_2O_3/Co_3O_4/AB	290	150	10	13	15	0.42

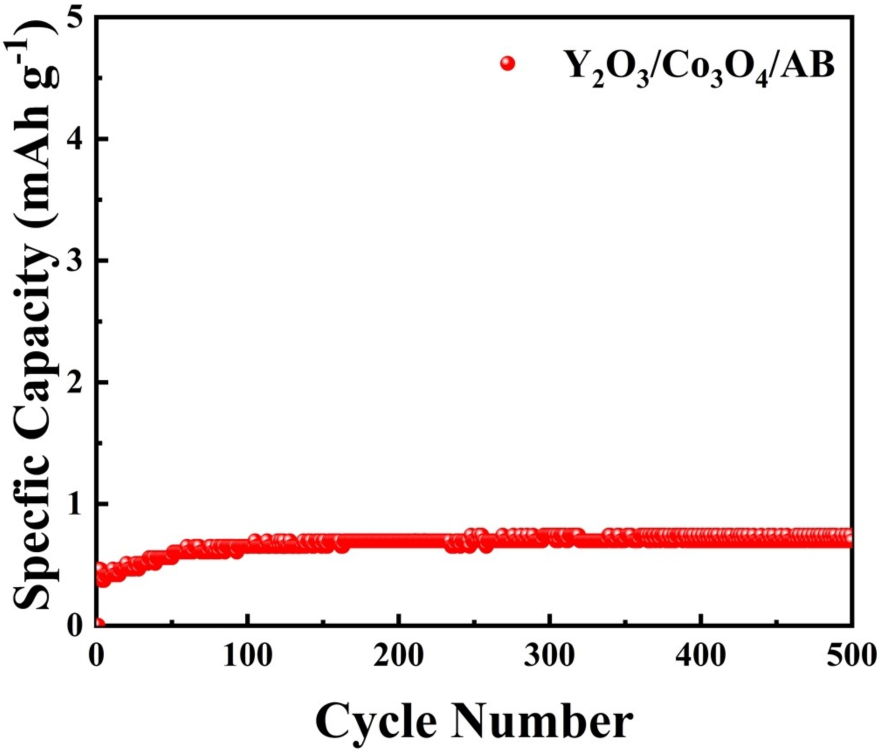

Figure.S6. The specific capacity of cell with the Y_2O_3/Co3O_4/AB heterostructure as the electrode and the lithium foil as the counter electrode.

Reference

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