Supporting Information

Red Phosphorus Confined in Hierarchical Hollow Surface-Modified Co_9S_8 for Enhanced Sodium Storage

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Experimental

Chemicals

cetyltrimethylammonium bromide (CTAB, 99%), tetraethoxysilane (99%), ammonia solution (25 wt%, AR), polyvinylpyrrolidone (PVP), cobalt acetate tetrahydrate (AR), ammonium chloride (AR, ≥99.5%)， sodium sulfide nonahydrate (AR,≥98.0%)was purchased from Sigma. All chemicals were used as received without further purification.

Synthesis of SiO_2 hollow spheres

A modified Stöber method was used to synthesize SiO_2 spheres with a diameter of about 400 nm. 0.16g CTAB (cetyltrimethylammonium bromide,99%), 1.5mL ammonia (25%) was dispersed into 120mL ethanol and 30mL H_2O. Subsequently, the solution was transferred to a three-necked flask, stirred vigorously, and 1.0 mL of tetraethoxysilane (99%) was slowly added. Then, the reaction was kept in a microwave synthesizer at a constant temperature of 60°C continuously stirred for 3 hours. The resulting precipitate was collected and washed several times with an absolute ethanol-HCl solution to remove CTAB, and finally dried under vacuum at 50 ° C for 12 hours.

Synthesis of Co-SiO_2 hierarchical hollow spheres

0.01 g of silica spheres were dispersed in 20 mL ethanol and 10 mL deionized water by stirring and ultrasound. After the SiO_2 was completely dispersed, 0.1 mmol Co $(CH_3COO)_2 \cdot 4H_2O$, 4 mmol NH_4Cl and 0.6 mL of ammonia were added to form a

solution. Then it was poured into a polytetrafluoroethylene reactor, heated to a certain temperature and kept. When the autoclave was cooled to room temperature, the pink precipitate was collected and washed several times with deionized water and dried under vacuum at 50 ° C overnight.

Characterization

XRD patterns are carried out using a Bruker D8 Advance X-ray diffractometer at 40 kV and 40 mA over 10° to 90° 2θ range with a Cu K_α radiation. Sample morphology is examined by a scanning electron microscope (AMRAY 1000B) and transmission electron microscope (TEM, JEM-2010). Scanning transmission electron microscopy has also been performed using high angle annular dark field (HAADF-STEM) detectors. Nitrogen adsorption-desorption measurements are conducted at 77 K on a Micromeritics Tristar apparatus. The specific surface area is determined following the Brunauer-Emmet-Teller analysis. Raman spectra were carried out on RM-1000 (Renishaw) with an excitation laser of 632.8 nm. The X-ray photoelectron spectroscopy (XPS) measurement was carried out on Thermo ESCALAB 250XI spectrometer.

Electrochemical measurements

For electrochemical performance evaluation, half-cell studies were performed. P@Co_9S_8 composites (70 wt.%) was used as the working electrode with Super P carbon (20 wt.%) and sodium alginate (10 wt.%) in deionized water to form a uniform slurry which was then applied on copper foil and dried in vacuum at 80 °C for 48 h. The loading mass of P@ Co_9S_8 is calculated to be 4.5 mg cm^{-2} and the coin-type cells using CR2025 were fabricated with 1 M $NaClO_4$ in ethylene carbonate/diethyl carbonate (1:1 vol.%) with 5wt.% fluoroethylene carbonate as the electrolyte, glass microfibers (Whatman) as separators and Na metal (Aladdin) as auxiliary electrodes. The coin cells are assembled in an argon-filled glove-box. The galvanostatic charge-discharge tests are at room temperature between 0.01 V and 2.0 V versus Na^+/Na by a Land 2100A tester. The cyclic voltammetry (CV) is performed on Princeton electrochemical workstation between 0.01 and 3.0 V with a scan rate of 0.1 mV s^{-1}.

Dissolution of sample

The red P, Co_9S_8 and P@Co_9S_8 with the same surface area of 1m^2 were added into 1.5ml of liquid electrolyte. The mass of the accurate red P, Co_9S_8 and P@Co_9S_8

composites added was determined by their respective specific surface areas. The samples were vigorously stirred and then kept standing for a month.

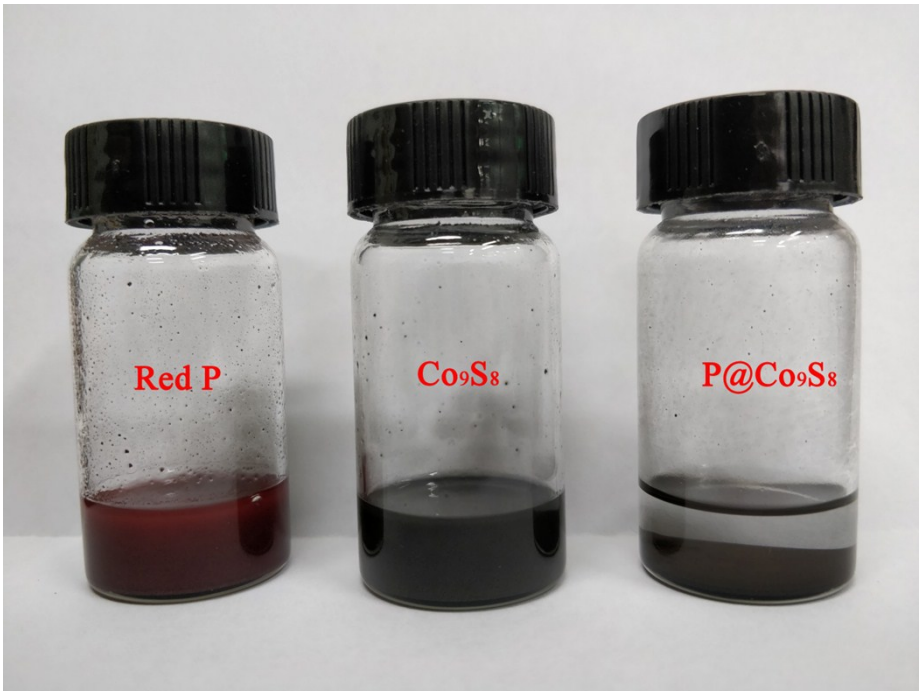

Figure S1. The solubility of red P, Co_9S_8 and P@Co_9S_8 in the liquid electrolyte.

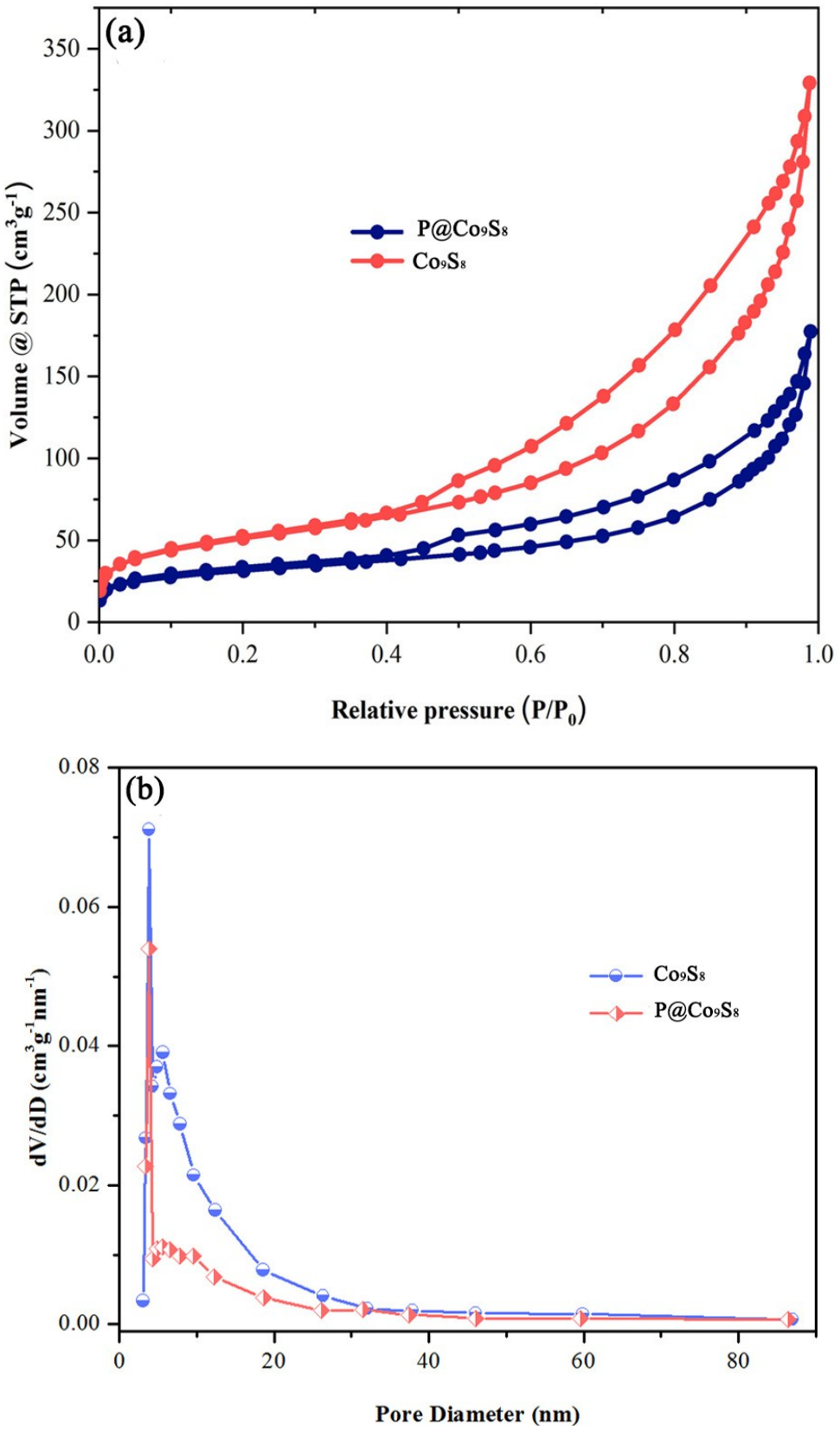

Figure S2 (a) Nitrogen adsorption-desorption isotherms, (b) Pore size distribution of P@Co_9S_8 andCo_9S_8.

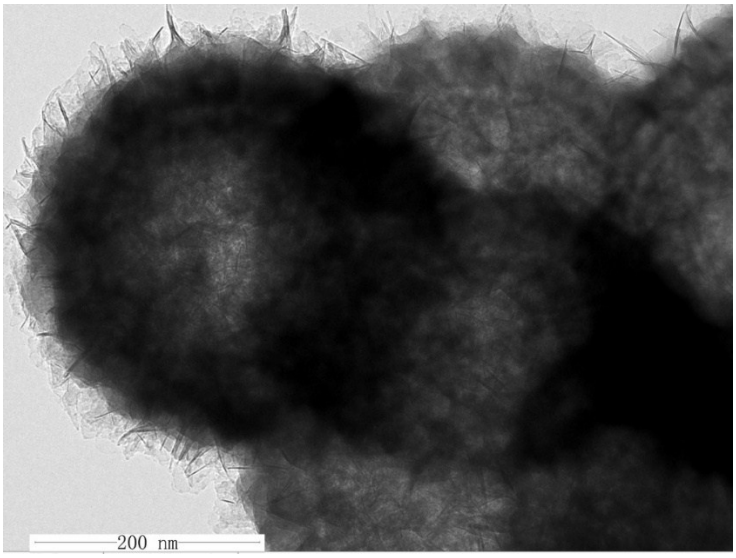

Figure S3 Detailed TEM image of P@Co_9S_8 electrode after 1000 cycles.

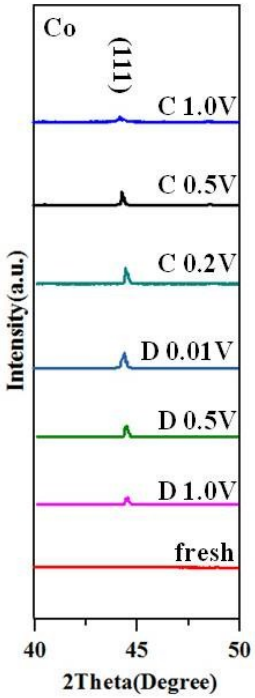

Figure S4 The *ex-situ* XRD of the discharge-charge profile of P@Co_9S_8 at different potentials for the 1st cycle at current density of 0.5 A g^{-1}.

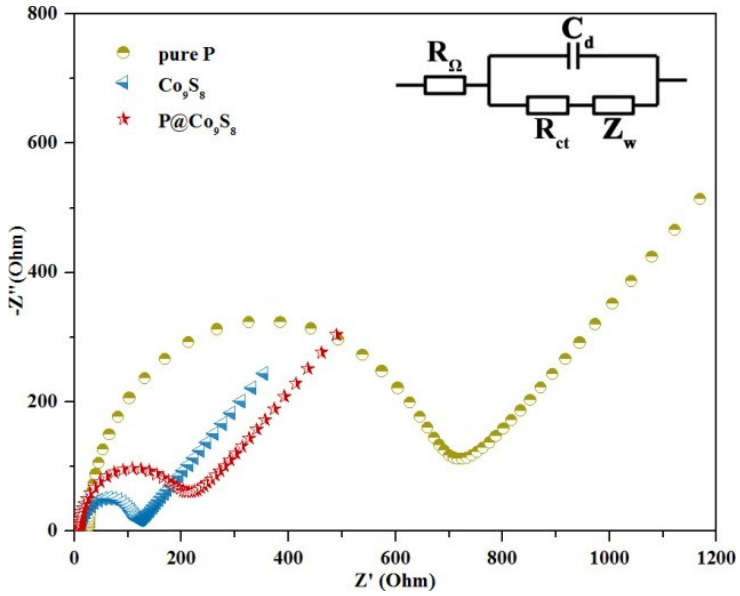

Figure S5 Electrochemical impedance spectroscopy of P, Co_9S_8 and P@Co_9S_8.

Table S1 Comparison of cyclic stability between the current P@Co_9S_8 composite anode and other representative red P based anodes in LIBs/SIBs.

Materials	Method	Red P content wt./%	Current density /A g^{-1}	Specific capacity /mAh g^{-1}	Ref
P-TiO_2-C	V/C	60	1	540 (after 100 cycles)	1
P@N-MPC	V/C	22.6	1.0	450 (after 1000 cycles)	2
SiC@graphene@RP	V/C	30.16	0.2	553 (after 100 cycles)	3
RP-SWCNT composite	V/C	60	0.5	560 (after 200 cycles)	4
P@RGO	Physical vapor position	61.4	1.6	914 (after 300 cycles)	5
RP/amorphous-TiO_2	Ball-milling	12.6	0.1	369 (after 100 cycles)	6
P@Co_9S_8	V/C	50	1	551.7 (after 1000 cycles)	Current study

Table S2 Fitted impedance parameters of Rs, Rct and W.

Electrode materials	$R_s(\Omega)$	$R_{ct}(\Omega)$	$W(\Omega)$
P	20.87	616.1	99.1
Co_9S_8	11.06	99.29	366.5
$P@Co_9S_8$	8.476	180.7	93.18

References

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