Electronic supplementary information

Electron-Delocalization Catalyzer for High Performance Low-temperature Li-S Batteries

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Experimental Sections

Synthesis of ODVO@PCN nanocomposites

ODVO@PCN was prepared via a solvothermal method followed by a hydrogen thermal reduction method. In detail, the purified multi-walled carbon nanotubes (CNTs) powder (180 mg) was dispersed into 75 mL deionized water under sonication to form homogeneous suspension, the NH_4VO_3 (278.4 mg) was added into 100 mL absolute ethyl alcohol under sonication to form homogeneous solution. The NH_4VO_3 solution was then dripped into the dispersion slowly under vigorous stirring. After that, the mixture was transferred into a Teflon-lined stainless-steel autoclave and heated to 180 °C for 24 h. After cooling to room temperature, the resultant solid product was collected by filtration, rinsed by deionized water repeatedly and freezing dried for 24 h. The VO@PCN nanocomposites were obtained by calcining the precursor at 700 °C for 2 h under an Ar (99.99%) atmosphere with a heating rate of 5 $^{o}C\ min^{-1}$. At last, the ODVO@PCN nanocomposites were generated after heat reduction of the VO@PCN at 500 °C for 2 h under an Ar/H_2 (5%:95%, by volume) mixture atmosphere.

Preparation of sulfur cathodes nanocomposites

The sulfur cathodes nanocomposites were prepared through in-situ liquid reaction method. The above synthesized ODVO@PCN (200 mg) was suspended in 600 mL deionized water under sonication till form uniform suspension. Sublimed sulfur (0.72 g) with $Na_2S{\cdot}9H_2O$ (1.82 g) was added into a 25 mL deionized water by stirring at room temperature to obtain Na_2S_x solution. Then, the homogeneous Na_2S_x solution (21 mL) was dripped into the above suspension slowly with strong magnetic stirring. Thereafter, HCOOH solutions (2 mol L^{-1}) was added slowly to the Na_2S_x infiltrated ODVO@PCN mixture for in-situ deposition of elemental S with overnight continuous stirring. The as-synthesized mixture was collected by filtration and washed by deionized water to remove the soluble impurities. After freezing dried for 24 h, the collected mixture was sealed in a vessel full of argon gas and heated at 155 °C for 12 h to fully infiltrate sulfur into the porous matrix to generate ODVO@PCN-S nanocomposites. The VO@PCN-S nanocomposites was fabricated using the same method.

Li-S full cell assembly

Upon a weight ratio of 7:2:1, the sulfur composite cathodes were prepared by mixing the as-synthesized nanocomposites, carbon black, and polyvinylidene fluoride (PVDF) as binder in an appropriate amount of N-methyl-pyrrolidinone (NMP) solvent under continuous stirring till forming uniform slurry. The fully mixed slurry was then coated on aluminum foil to form an even layer by a film blade using a thickness of 200 μm, which was dried in a vacuum oven at 60 °C over 24 h. The prepared electrode was punched into discs of 12 mm in diameter. The Li-S cells were assembled with ODVO@PCN-S discs cathode (12 mm), and Li anode separated by Celgard 2350 commercial separator, adding the electrolyte (1 M LiTFSI with 1 wt% $LiNO_3$ dissolved in mixed solvent of DME/DOL in volume ratio of 1:1) according to the electrolyte/sulfur (E/S) ratio of 15 μL mg^{-1}.

Materials and cells characterization

The X-ray diffraction (XRD) was carried out on an XRD-7000S X-ray diffractometer with Cu-Ka radiation (λ=0.15418 nm) within a 2θ range of 10°~80°. X-ray photoelectron spectra (XPS) were collected on an AXIS ULTRA system. Nitrogen absorption and desorption isotherms were recorded on an ASAP 2020 (Micromeritics). Raman spectra were performed on a Horiba Laser Raman spectrometer (EUROVECTOR EA3000). Thermal gravimetric analysis (TGA) was conducted on a TG/DTA 6200 setup with a heating rate of 10 °C min^{-1} under nitrogen flow or air atmosphere. Scanning electron microscopy (SEM) images were observed using a Germany MERLIN Compact Scanning Electron Microscope (Zeiss). Transmission electron microscopy (TEM) samples were imaged using a JEM-3010 Transmission Electron Microscope. The electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed with a VMP-3 potentiostat/galvanostat station. The other electrochemical evaluations on cells were performed on a Neware battery testing system (BTS-5 V 10 mA) within the voltage window of 1.6~2.8 V at different current rates.

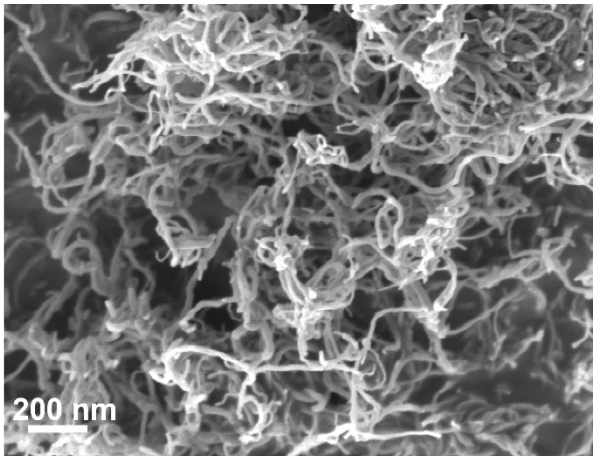

Figure S1 SEM image of the VO@PCN nanocomposite.

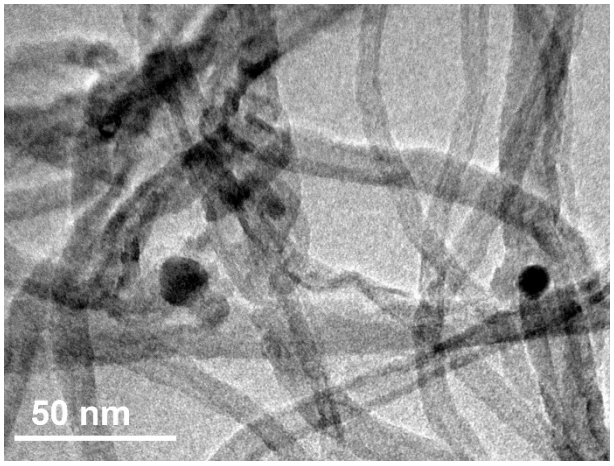

Figure S2 TEM image of the VO@PCN nanocomposite.

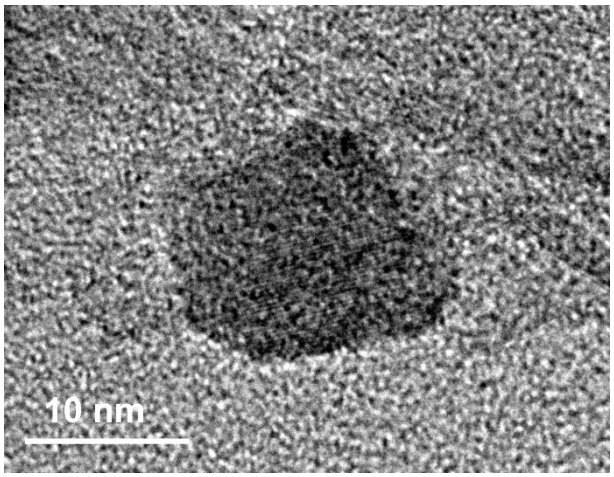

Figure S3 HRTEM image of the ODVO@PCN nanocomposite.

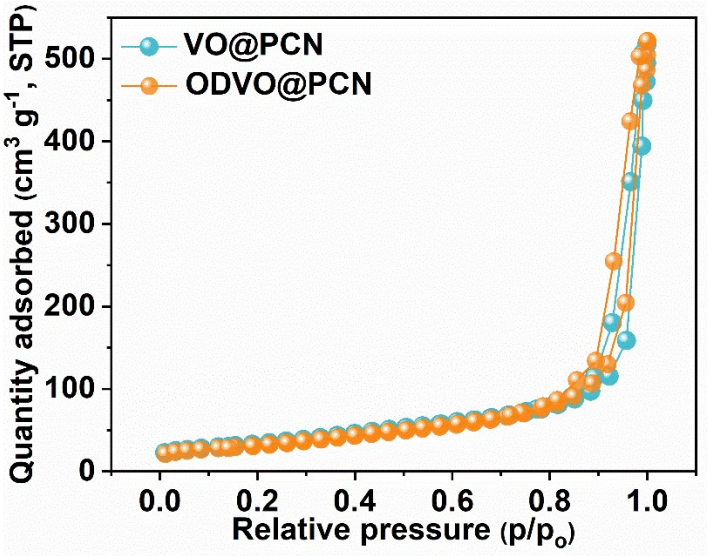

Figure S4 N_2 adsorption/desorption isotherms of the ODVO@PCN and VO@PCN nanocomposites.

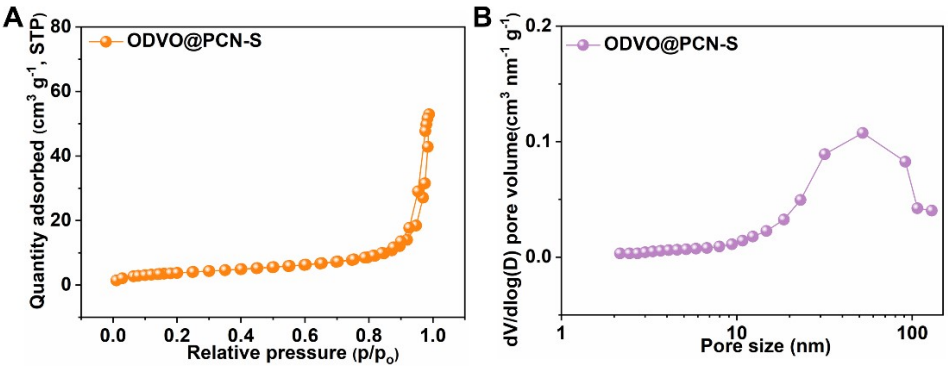

Figure S5 (A) Nitrogen absorption/desorption isotherms and (B) pore size distribution of the ODVO@PCN-S nanocomposite.

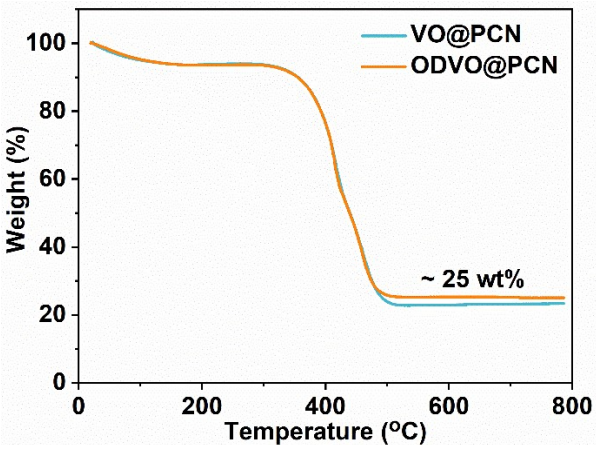

Figure S6 TGA curves of the ODVO@PCN and VO@PCN nanocomposites.

Figure S6 displays TGA curves of the ODVO@PCN and VO@PCN nanocomposites under air atmosphere with heating rate of 10 °C min^{-1}, presenting that the ODVO@PCN experiences a fast weight loss of about 75 wt.% between 300~500 °C. Finally, 25% of the nanocomposite is remained. According to the reaction formula:

$$V_2O_3 + O_2 \xrightarrow{High\ temperature} V_2O_5$$

In theory, the weight of the pure V_2O_3 increases to nearly 1.21 times due to the transformation from V_2O_3 to V_2O_5 under the high temperature heating with O_2 atmosphere. Therefore, it could be deduced that the remained mass after the TG analysis in **Figure S6** should be ascribed to the final existence of V_2O_5, which was corresponded to be about 20.6% (25% / 1.21) of V_2O_3. This experimental result matches quite well with the nominal designed ratio of V_2O_3.

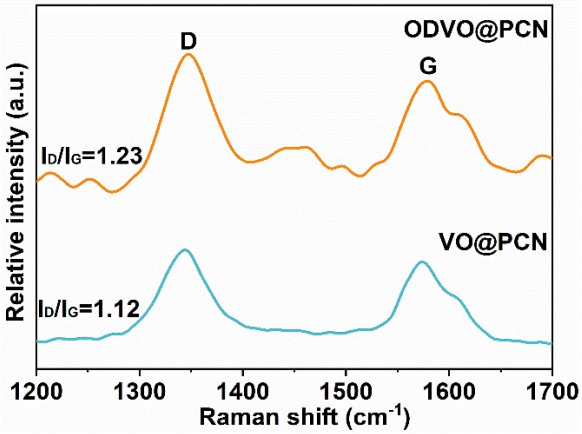

Figure S7 The D and G peaks in Raman spectra of the ODVO@PCN and VO@PCN nanocomposites.

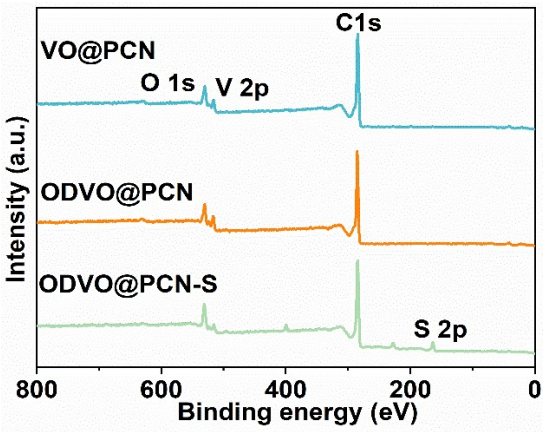

Figure S8 XPS survey spectra of the ODVO@PCN, ODVO@PCN-S and VO@PCN nanocomposites.

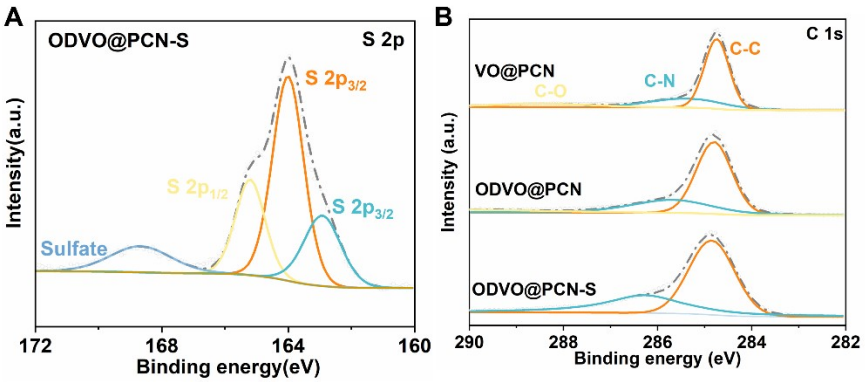

Figure S9 High-resolution spectra of (A) S 2p of the ODVO@PCN-S nanocomposite and (B) C 1s of the ODVO@PCN, ODVO@PCN-S and VO@PCN nanocomposites.

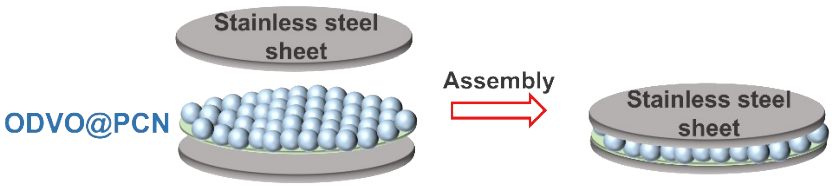

Figure S10 Schematic depiction of assembly of block cells for the measure of the ionic conductivity.

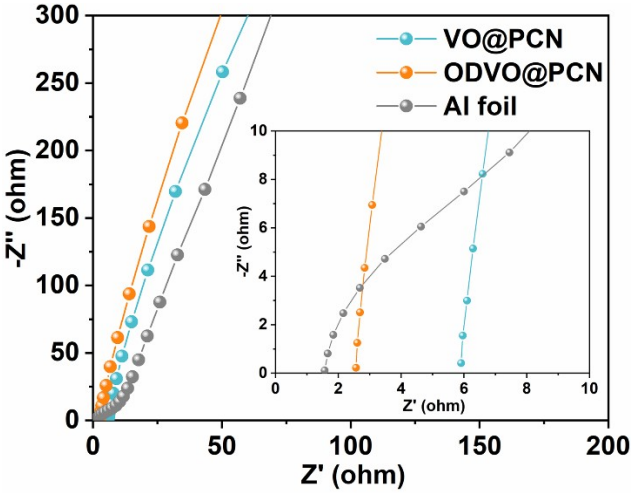

Figure S11 Electrochemical impedance spectroscopy (EIS) spectra recorded on the block cells with ODVO@PCN and VO@PCN electrode.

In detail, the block cell is assembled by sandwiching ODVO@PCN between two stainless steel sheets (**Figure S10**). Then, the ion conductivity (σ) was tested on the block cells and calculated on the following formula:

$$\sigma = \frac{L}{R_b S}$$

where L represents the thickness of the modulation layer, R_b is the resistance of the coating layer recorded by the electrochemical impedance spectroscopy (EIS) spectra in **Figure S11**, and S is the effective area of the layer.

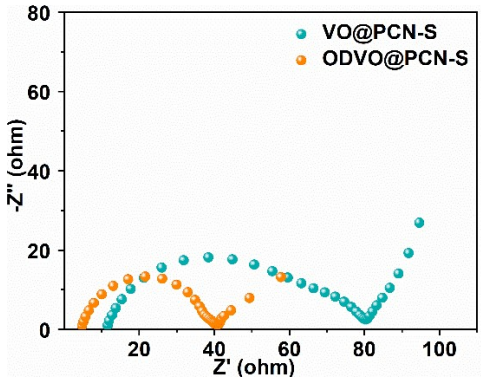

Figure S12 Comparison of EIS between the ODVO@PCN-S and VO@PCN-S electrodes after cycling.

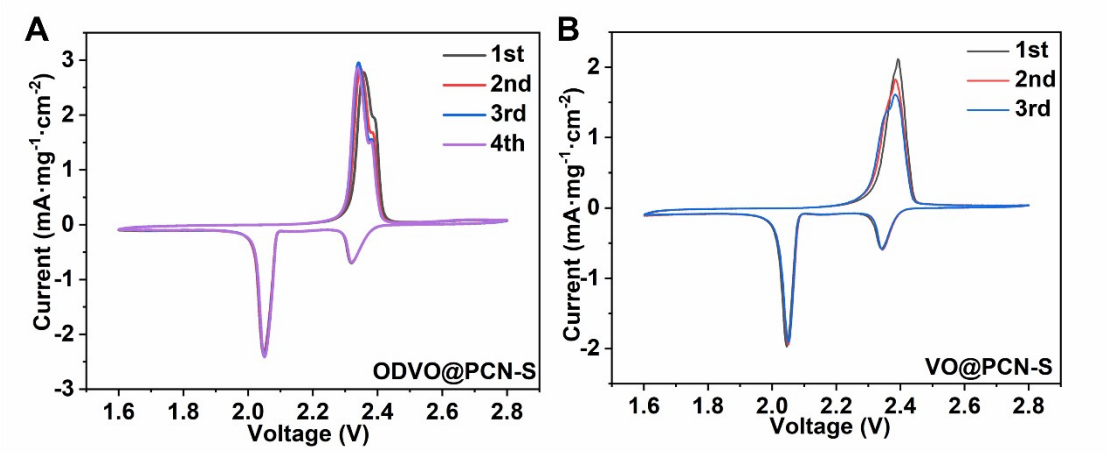

Figure S13 CV profiles of (A) ODVO@PCN-S and (B) VO@PCN-S cathodes in the first few cycles scanning at 0.1 mV s^{-1}.

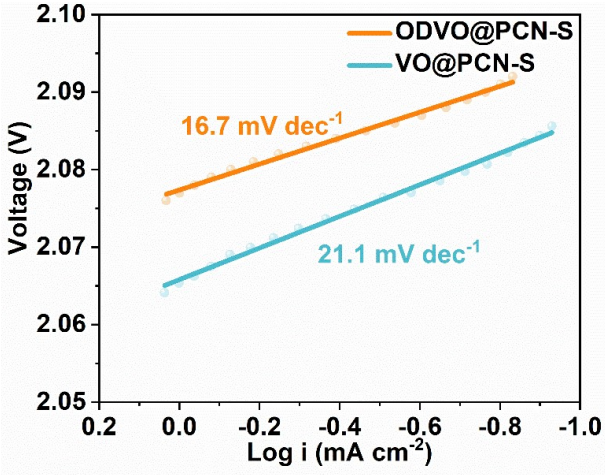

Figure S14 Tafel plots of different cathodes derived from corresponding initial CV curves at the scan rate of 0.1 mV s^{-1}.

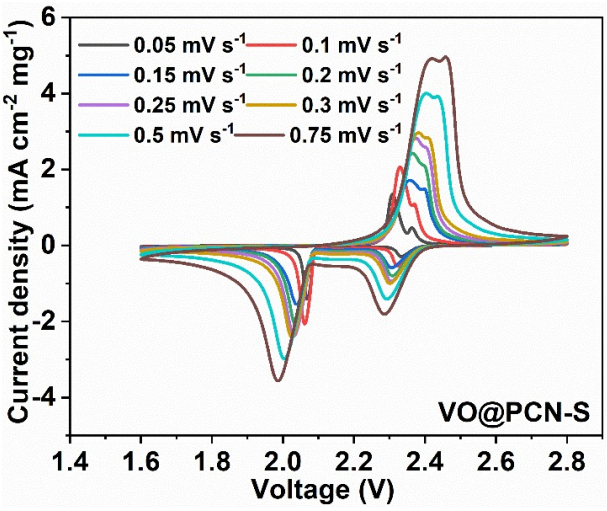

Figure S15 Scan rate-dependent CV curves on the VO@PCN-S cathode.

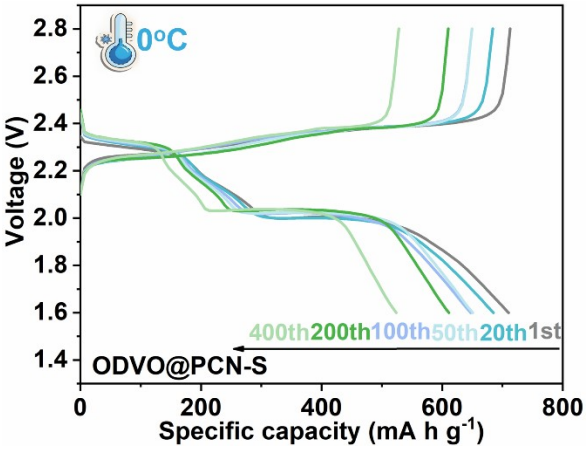

Figure S16 Voltage-capacity profiles on the ODVO@PCN-S cathode cycled at 0.5 C under 0 °C.

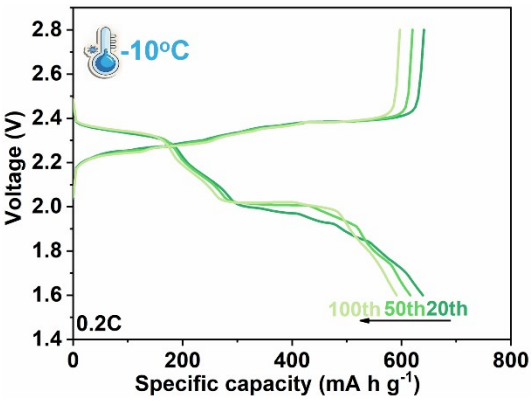

Figure S17 Voltage-capacity profiles on the ODVO@PCN-S cathode cycled at 0.2 C under -10 °C.

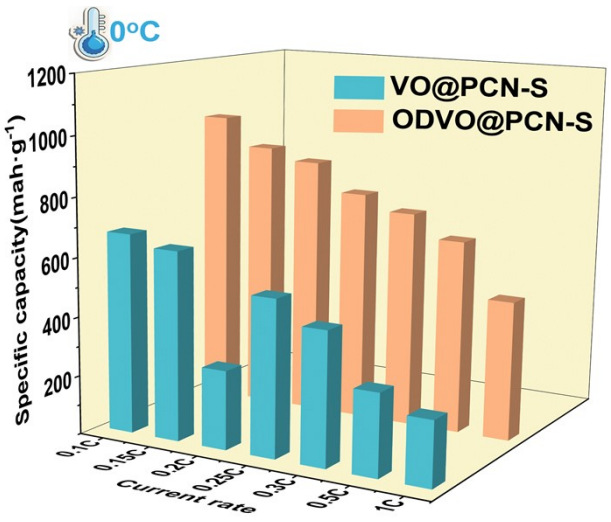

Figure S18 Capacity comparison on the ODVO@PCN-S and VO@PCN-S cathodes at various current rate under low temperature of 0 °C.

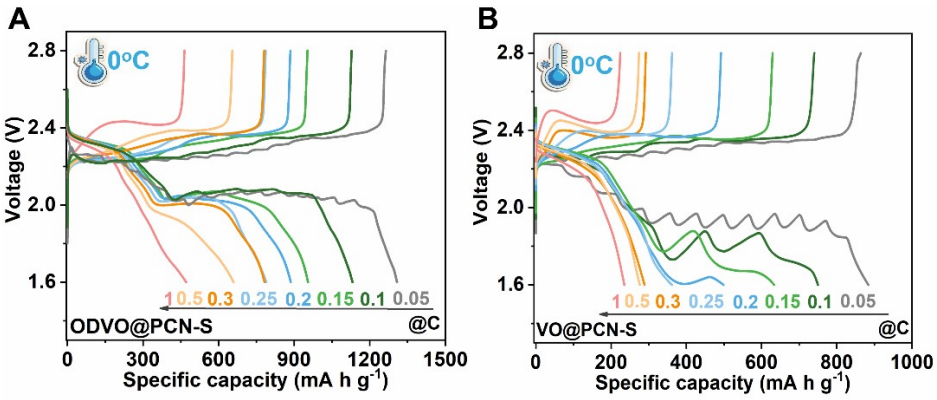

Figure S19 Voltage-capacity profiles on the ODVO@PCN-S and VO@PCN-S cathodes depending on current rate under low temperature of 0 °C.

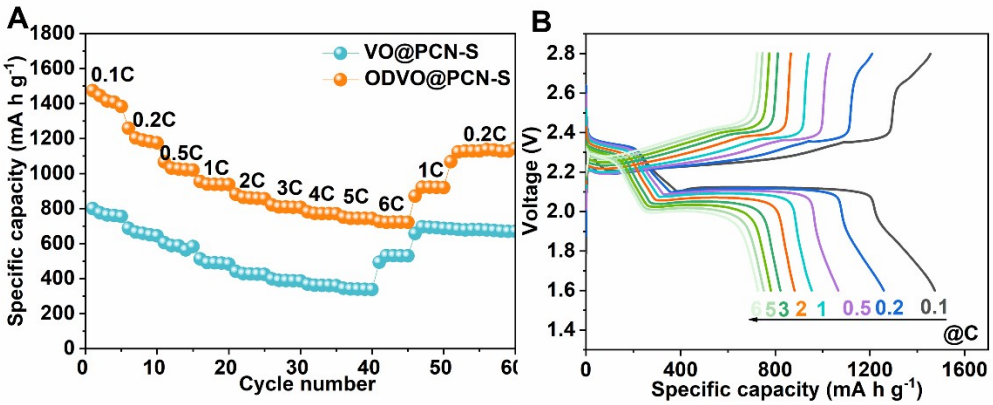

Figure S20 (A) Rate performance of the two cathodes and (B) Voltage-capacity profiles on the ODVO@PCN-S cathode depending on current rate under room temperature.

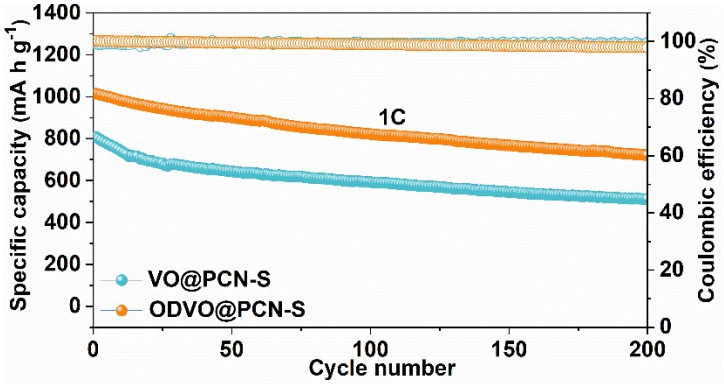

Figure S21 Cycle performance of the ODVO@PCN-S and VO@PCN-S cathodes at 1C under room temperature.

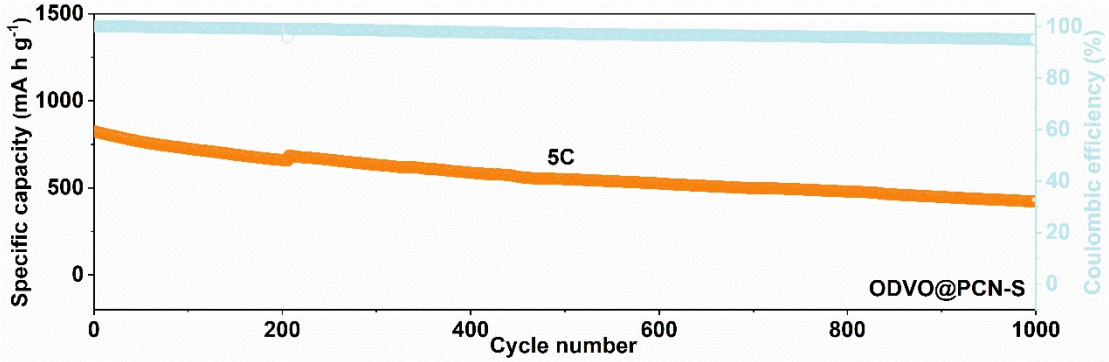

Figure S22 Cycle performance of the ODVO@PCN-S cathode at 5C under room temperature

Table S1 Comparison of electrochemical performance of the ODVO@PCN-S cathode with that reported in recent literatures.

Cathodes	Synthesis method	High-rate performance (mA h g^{-1})	Cycling performance and retention	Cycle number	Temperature (°C)	References
ODVO@PCN-S	**Hydrothermal reaction and hydrogen treatment**	**521 (1C)**	**710 (90.7%, 0.5C)** **892 (64.5%, 0.2C)**	**400 (0.5C)** **100 (0.2C)**	**0 (0.5C)** **-10 (0.2C)**	**This work**
MB-VN modified separator	Solvothermal method and pyrolysis under NH_3 atmosphere	800 (0.2C)	649 (85.2%, 1C)	100	-10	*ACS Nano,* 2023, *17*, 11527.
Mo_6S_8/S	Ball milling	800 (0.2C)	/	/	0	*Small, 2023, 19, 2300042.*
EPDB-CgCP	Chemical assembly with phosphorization reaction in Ar atmosphere	/	972 (66.6%, 0.1C)	80	0	*Adv. Funct. Mater., 2023, 33, 2302624.*
Ni@C/graphene modified separator	Hydrothermal reaction and Argon gas treatment	/	403 (87.8%, 0.1C)	200	-40	*Adv. Energy Mater. 2020, 10, 2000907.*
Li_2S_6/FCN-MO@CNFs	Impregnation and pyrolysis under Ar/H_2 atmosphere	278.7 (10C)	1000 (90.5%, 0.2C)	100	-10	*Chem. Eng. J., 2023, 458, 141445.*
TiO_2@C@CSC	Hydrothermal reaction and H_2/Ar treatment	138 (1C)	649 (51%, 0.2C)	250	-20	*ACS Sustain. Chem. Eng., 2023, 11, 3657.*
PAN@S	Pyrolysis under N_2 atmosphere	/	453 (99.2%, 0.1C)	50	-10	*J. Energy Chem., 2020, 51, 154.*