Electronic Supplementary Information

Thermotolerant and Li$_2$S$_n$-Trapped/Converted Separators Enabled by NiFe$_2$O$_4$ Quantum Dots/g-C$_3$N$_4$ Nanofiber Interlayers: Toward More Practical Li-S Batteries

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1. Experimental Section

1.1 Synthesis of *g*-C$_3$N$_4$ nanofibers and NiFe$_2$O$_4$ QDs

For typical synthesis of g-C$_3$N$_4$ nanofibers, 2.5 g melamine (Sigma-Aldrich) is dissolved into a 160 mL mixed solution made of ethylene glycol and water in a volume ratio of 2:1 at 60 °C. Afterwards, 60 mL 0.3 M HNO$_3$ is dropwise added. The obtained mixture is then aged for 20 min, placed into a

refrigerator at -15 °C and kept still for 1h. Later, the white precipitates are filtered, washed by deionized water several times, and dried in 60 °C electrical oven overnight. Finally, the powder samples are then collected, put into a N_2 filled tube furnace and calcined at 500 °C (heating rate: 5 °C /min) for 2 h. After cooled down naturally, g-C_3N_4 samples with a light-yellow color are fetched for later use.

As for $NiFe_2O_4$ QDs preparation, 4.04 g $Fe(NO_3)_3 \cdot 9H_2O$ (purity>99.99%, Sigma-Aldrich) and 1.45 g $Ni(NO_3)_2 \cdot 6H_2O$ (purity>99.99%, Alfa) are dissolved within 80 mL deionized water to form a homogeneous solution. Next, the concentrated ammonia (Sigma-Aldrich) is slowly added until the solution pH value reaches 8. The obtained transparent solution is subsequently transferred into a Teflon liner, which is sealed into a stainless steel autoclave, heated to 190 °C in an electrical oven and kept for 10h. After cooled down to room temperature naturally, brown $NiFe_2O_4$ QDs powders are collected by centrifugation, washed with deionized water several times and dried at 60 °C overnight.

1.2 Preparation of $NiFe_2O_4$ QDs@g-C_3N_4 Nanofibers Modified Separators

Typically, 10 mg g-C_3N_4 nanofibers and 10 mg $NiFe_2O_4$ QDs are added into a 20 mL mixed solution containing water and ethanol (volume ratio=1:1). Such a mixture is then ultrasonically treated for 30 min, and dried at 60 °C to obtain $NiFe_2O_4$ QDs@g-C_3N_4 hybrid products. Next, these powder samples, carbon black (CB; Ketjenblack EC-300J) and polyvinylidene fluoride (PVDF, Sigma-Aldrich) are mixed in a weight ratio of 6:3:1 and ground in moderate N-methylpyrrolidinone (NMP; Fluka) solvent to form a uniform slurry. This mud-like slurry is then pasted onto polypropylene (PP; Celgard 2500) separators by a paint scraper and dried at 60 °C in vacuum for 12 h. For comparison study, the g-C_3N_4 slurry is also prepared and coated onto PP separators by according to the same procedures

aforementioned.

1.3 Materials Characterization and Electrochemical Testing

The crystalline structure/elemental information of samples are detected by X-ray diffraction (XRD, Bruker D8 Advance diffractometer with Cu Kαradiation, λ=1.5418 Å) and energy dispersive X-ray spectroscopy (EDS). Also, the X-ray photoelectron spectroscopy (XPS, PerkinElmer model PHI 5600 spectrometer) is used to probe more elemental information on samples surface. The basic geometric morphology and crystal structures of samples are characterized using a field-emission scanning electron microscope (FESEM, JEOL JSM-7800F) and transmission electron microscope (TEM, JEM 2010F). The N_2 adsorption/desorption data are recorded at a temperature of 77 K using a Autosorb-IQ2-MP-C system. Prior to this testing, the powder samples are degassed at 120 °C under vacuum for 12h. The specific surface area is calculated according to the Brunauer-Emmett-Teller (BET) equation, and the pore volumes are calculated from the adsorbed N_2 amount at a relative pressure (P/P_0) of 0.99. The pore-size distributions are measured by referring to a nonlocal density functional theory (NL-DFT) model. The Kruss contact angle tester (DSA10-Mk2, Germany) is further used to measure the contact angles between the electrolyte and different separators.

The S/CB composites (S: CB=9:1) are used as working actives in cathodes. The electrode powders are then mixed with CB and PVDF binder under a weight ratio of 8:1:1 in NMP to form a uniform slurry. This slurry is then pasted onto an Al foil evenly and dried at 60 °C in vacuum overnight. The gained cathodes in an S loading range of 2.5-2.8 mg/cm^2 are then cut into discs. Besides, cathodes with a higher S areal density of 6.24 mg/cm^2 are also made for testing. 2032-type coin cells are assembled with S/CB cathodes, $NiFe_2O_4$ QDs@g-C_3N_4 modified separators and Li foil anodes in an Ar-

filled glovebox (Mikrouna; H_2O<0.1 ppm, O_2<0.1 ppm). The electrolyte is prepared by dissolving 1M

bis(tri-fluoromethane) sulfonamide lithium salt (LiTFSI) into a DOL/DME (*vol%*=1:1) mixed solvent

containing 1 *wt%* $LiNO_3$. The electrolyte/S (E/S) ratio is controlled to be a level of ~4.26 µL/mg. For

battery testing, the cyclic voltammetry (CV) measurements (voltage range: 1.7-2.8 V *vs.* Li/Li$^+$) and

electrochemical impedance spectroscopy (frequency range: 100 kHz-0.1Hz) are performed on a

CS310 electrochemical workstation. The galvanostatic charge-discharge tests are conducted by

NEWARE battery testers in a voltage window of 1.7-2.8 V (*vs.* Li/Li$^+$) at 25 ^{o}C.

As for Li_2S_6 adsorption testing, 2 mM Li_2S_6 solution is made by a synproportionation reaction of

Li_2S and S (molar ratio=1:5) in DOL/DME solvents. This testing is then carried out by soaking 20 mg *g*-

C_3N_4 or $NiFe_2O_4$ QDs@g-C_3N_4 powders into Li_2S_6 solution. The LiPS adsorption capability for different

powders is evaluated by UV-Vis spectroscopy (UV-1800, Shimadzu, Japan). To visualize the LiPS

adsorption effects for distinct interlayers, U-shaped glass bottles are utilized. Additionally, LiPSs

symmetric cells are used to examine the catalytic reaction kinetics of samples. Two identical

electrode disks (diameter: 12 mm; made of *g*-C_3N_4 or $NiFe_2O_4$ QDs@g-C_3N_4) are assembled into a

CR2032 coin-type cell with a PP separator and 30 µL 2 M Li_2S_6 electrolyte. To study the variations at

the separator-anode interfaces, Li/Li symmetric cells are also assembled using PP or $NiFe_2O_4$ QDs@g-

C_3N_4/PP separators, respectively.

1.4 Theoretical simulation and Calculations

The Li_2S_6 adsorption simulation and density functional theory (DFT) calculations based on the

Vienna ab initio simulation package (VASP) are performed through the *MatCloud+* platform. The

core−valence interaction is represented using the projector-augmented wave (PAW) method. The

plane wave energy cutoff is set to 450 eV. We also use the generalized gradient approximation with

the Perdew–Burke–Ernzerhof exchange-correlation functional and local Hubbard term U correction.

The Brillouin zone is sampled at the γ-point with $3 \times 1 \times 1$ k-point meshes for g-C_3N_4 model. The

energy and force criteria for the convergence of electron density are successively set to 10^{-5} eV and

0.05 eV $Å^{-1}$. The 2×2 supercell of g-C_3N_4 is used for the Li_2S_6 molecule adsorption. A vacuum gap of

12 Å is then set to restrict the interactions between periodic slabs.

2. Characterizations and additional testing results:
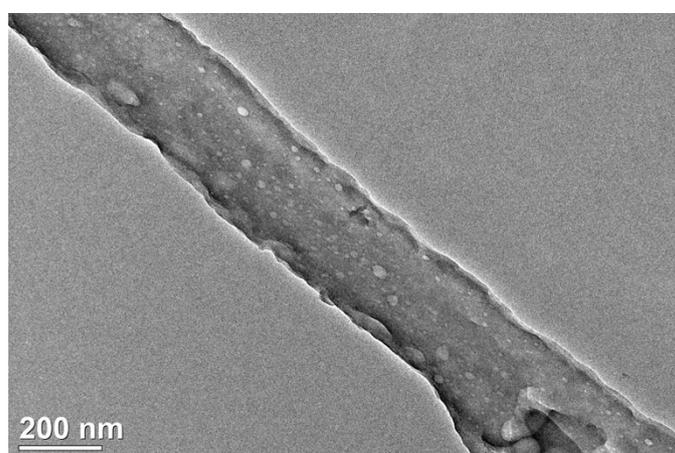
Fig. S1 The typical TEM observation on our synthesized g-C_3N_4 nanofibers.
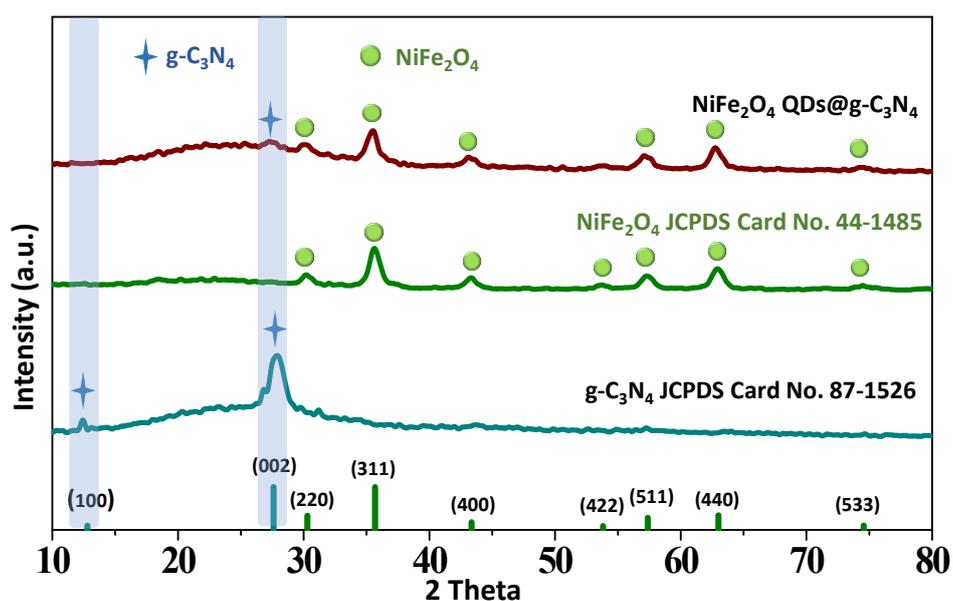
Fig. S2 XRD patterns of g-C_3N_4 nanofibers, $NiFe_2O_4$ QDs and $NiFe_2O_4$ QDs@g-C_3N_4 nanofibers.
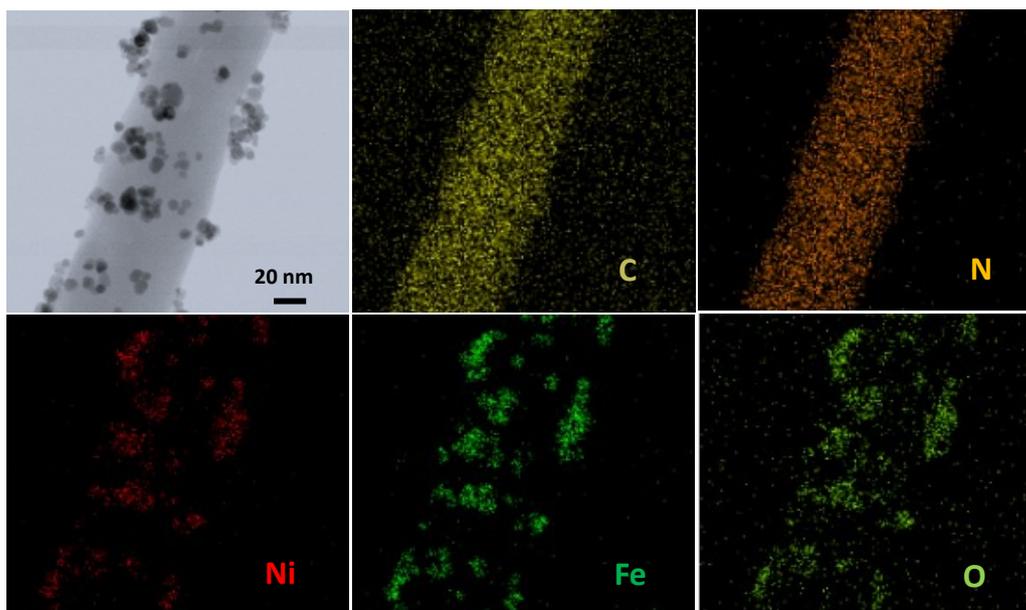
Fig. S3 The EDS elemental mapping result of NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$ nanofibers.
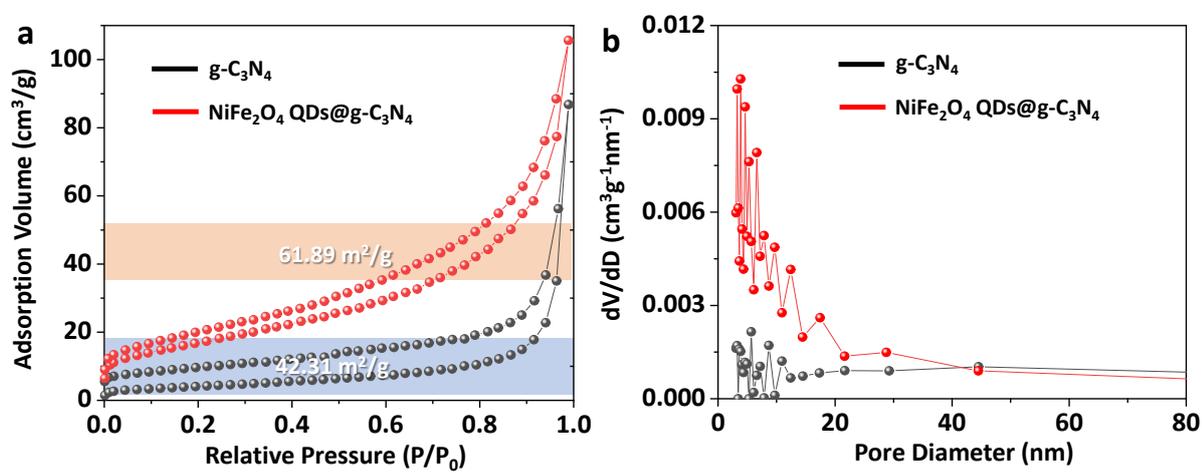
Fig. S4 (a) N$_2$ adsorption/desorption isotherm and (b) pore-size distribution plots of g-C$_3$N$_4$ and NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$ nanofibers.
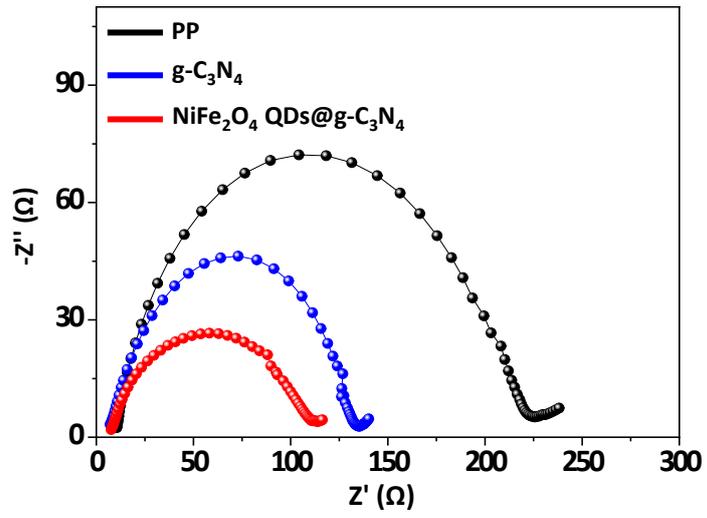
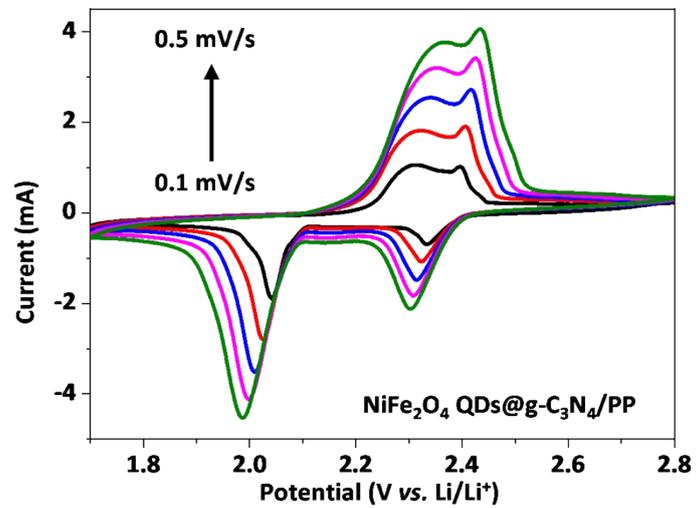**Fig. S5** Nyquist plots of LSBs configured by distinct separators.

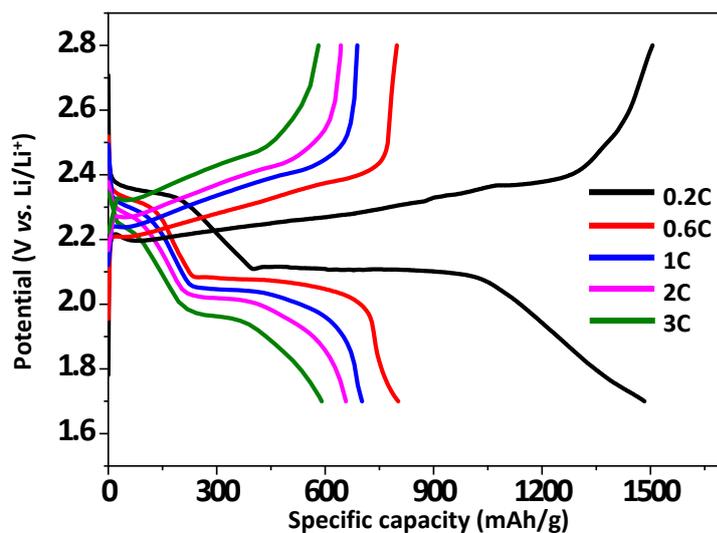**Fig. S6** CV curves of LSBs packed by NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$/PP under varied scan rates.

Fig. S7 Charge/discharge voltage profiles of LSBs made by $NiFe_2O_4$ QDs@g-C_3N_4/PP separators.
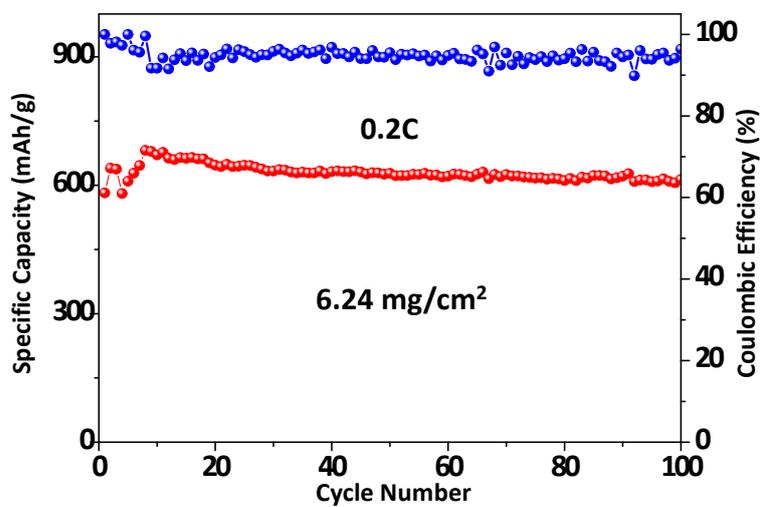

Fig. S8 Cyclic performance of LSBs assembled with $NiFe_2O_4$ QDs@g-C_3N_4/PP separators under a high S loading ratio of 6.24 mg/cm².
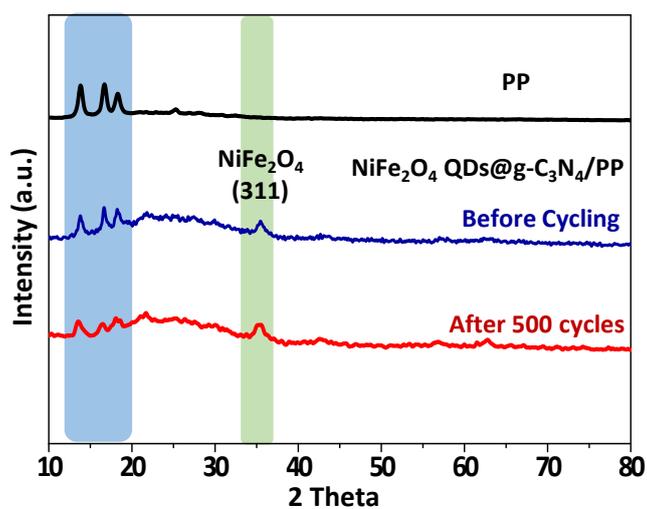
Fig. S9 XRD patterns of PP and NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$/PP separators before and after 500 cycles.
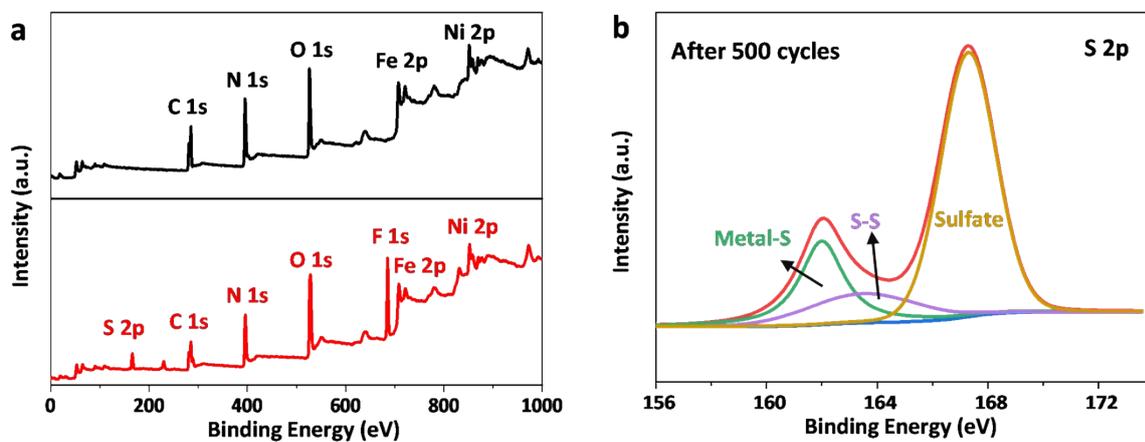

Fig. S10 (a) XPS survey spectra of NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$/PP separators before and after 500 cycles. (b) XPS S 2p spectrum of the cycled NiFe$_2$O$_4$ QDs@g-C$_3$N$_4$/PP separator.