Curtailing Carbon Usage with Addition of Functionalized NiFe$_2$O$_4$ Quantum Dots: Toward More Practical S Cathodes for Li–S Cells

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ABSTRACT

Smart combination of manifold carbonaceous materials with admirable functionalities (like full of pores/functional groups, high specific surface area) is still a mainstream/preferential way to address knotty issues of polysulfides dissolution/shuttling and poor electrical conductivity for S-based cathodes. However, extensive use of conductive carbon fillers in cell designs/technology would induce electrolytic overconsumption and thereby shelve high-energy-density promise of Li–S cells. To cut down carbon usage, we propose the incorporation of multi-functionalized NiFe$_2$O$_4$ quantum dots (QDs) as affordable additive substitutes. The total carbon content can be greatly curtailed from 26% (in traditional S/C cathodes) to a low/commercial mass ratio (~5%). Particularly, note that NiFe$_2$O$_4$ QDs additives own superb chemisorption interactions with soluble Li$_2$Sn molecules and proper catalytic features facilitating polysulfide phase conversions and can also strengthen charge-transfer capability/redox kinetics of overall cathode systems. Benefiting from these intrinsic properties, such hybrid hybrid...
cathodes demonstrate prominent rate behaviors (decent capacity retention with ~ 526 mAh g⁻¹ even at 5 A g⁻¹) and stable cyclic performance in LiNO₃-free electrolytes (only ~ 0.08% capacity decay per cycle in 500 cycles at 0.2 A g⁻¹). This work may arouse tremendous research interest in seeking other alternative QDs and offer an economical/more applicable methodology to construct low-carbon-content electrodes for practical usage.

**KEYWORDS** Carbon usage reduction; NiFe₂O₄ quantum dots; Additive substitute; Practical S cathode; Li–S cells

1 Introduction

Increasing demands for emerging electric vehicles and surplus electricity storage have trigger searches for next-generation energy-storage systems. Nowadays, Li–S cells are extremely admirable and encouraging given their great theoretical gravimetric/volumetric capacities, good environmental benignity, and pretty low cost due to abundant natural reserves of S [1–3]. Unfortunately, their practical applications are put off by three major constraints including: (i) inferior conductivity of either S/Li₂S cathodes or their intermediate/end-discharge products (causing sluggish redox reaction kinetics and less actives utilization ratio), (ii) huge volume expansions (e.g., ≈ 80% for S cathode) and notorious Li dendrite formation (undermining their long-term electrochemical stability/cyclic lifespan), and (iii) intractable polysulfide dissolution in organic electrolytes (inducing irreversible capacity decay and unstable Coulombic efficiency) [4, 5]. Aimed at tackling the above challenges, one prioritized strategy is the combination of functionalized carbonaceous frameworks (made up of hierarchically porous graphene, biomass-derived microporous carbon, or metallic organics [6–8]) with S or Li₂S to offset the electrode conductivity and operation stability [9, 10]. However, once the amount of such carbon fillers reaches a critical value of 50 wt% in cathodes, there would give rise to many troublesome issues for real applications [11]. Primarily, overusing carbons with large specific surface areas (100–1500 m² g⁻¹) and low tap density (0.1–0.3 g cm⁻³) results in a sponge-like cathode that requires flooded electrolyte to sufficiently wet all electrode regions. This predicatively intensifies the electrolyte-to-sulfur (E/S) ratio and battery weight, thereby diminishing the total cell specific energies [12]. Additionally, carbons’ hydrophobicity is adverse to organic electrolyte wettability, resisting Li⁺ transport at the solid–liquid interface and deteriorating the cell kinetics. Standing on internal chemical interactions, nonpolar carbon species are incomparable to work with polar polysulfides for long cyclic stability and capacity retention [13]. For commercial concerns of Li–S cells, scientists require to introspect shortcomings in current cell technology and devote to seeking for other feasible/rational solutions.

The use of functionalized quantum dots (QDs) with a typical sub-30 nm size (comparable to that of carbon black conducting agent) may be a better option due to their great volume-to-surface ratio, far less invalid pore volumes, high specific surface energy, and enriched dangling bonds beneficial for chemical adsorption. For example, Xu et al. once employed a very small amount of black phosphorus QDs as electrocatalysts, which can adsorb soluble polysulfide intermediates and meantime promote their conversions into solid-state Li sulfides due to numerous catalytic anchors on QDs edges. The integrated hybrid cathodes showcase rapid reaction kinetics without evident shuttling effects, showing a slow capacity decay rate (~ 0.027% per cycle) among all 103 cycles [2]. Park et al. reported the addition of graphene QDs into S cathodes can induce the formation of hierarchically functionalized S/carbon hybrids aided by involved O-rich groups on QDs. The robust C-S bonding can minimize irreversible losses of polysulfide anions, enabling good capacity retention (~ 1000 mAh g⁻¹ after 100 cycles at 0.5 C) and fast charge-transfer behaviors (remarkable discharge capacity of ~ 540.17 mAh g⁻¹ at 10 C) [14]. Hence, alternatively utilizing QDs would be highly useful for Li–S cells operation, which holds great promise in reducing carbon usage amount, thus lowering the electrolyte consumption and ensuring gravimetric/volumetric specific energies of devices.

Some transitional metal oxides have been paid special attention as both physicochemical adsorbers for Li polysulfide intermediates and good catalysts to boost long-chain Li₂Sn (n = 3–8) conversion into insoluble species and meantime accelerate substance transitions forward solid-date Li₂S/Li₂S₂ [15, 16]. Ferruginous oxide families (e.g., FeO, Fe₂O₃, Fe₃O₄), the most economical and welcome material candidates, own favorable chemical bonding to polysulfide molecules and obey reversible adsorption/
desorption mechanism based on strong polar surface or Lewis acid—base interactions [17–19]. Another recognized prototype material should be designated to Ni-based oxides (e.g., Ni2O3, NiO, β-NiOOH), which can speed up redox reaction kinetics aided by their superb electrocatalytic activities deriving from their surface/sub-surface defects or vacancies [20–22]. As a mixed combination of Fe and Ni oxides, NiFe2O4 might be a better choice than aforementioned since it would not only anchor dissociative polysulfide species and suppress the adverse “shuttling effect” during charge/discharge procedures, but also promote cell kinetics thanks to its positive catalytic properties (e.g., expediting sulfide redox couples S2−/S8− conversion) [23]. The extra incorporation of semi-conducting NiFe2O4 (conductivity: 74.32 S cm−1) into cathode systems would further reinforce the electrons-transfer capability of entire electrode systems.

We herein attempt to minimize the total carbon usage by alternative use/addition of multi-functionalized NiFe2O4 QDs with a characteristic fluorescence effect at 568 nm (excitation wavelength: 325 nm, see Fig. S1) into cathode systems, aiming at building more efficient and practical Li–S cells. The implanted NiFe2O4 QDs are able to serve as “modular building blocks” in optimized electrodes for Li2S localization/catalysis because of their good electrical conductivity and ample anchoring sites on external surface. The as-configured cathodes would not only own a proper ability of inherent chemisorption/interactions with polysulfides but also fast charge-transfer and redox reaction kinetics. Particularly, note that by choosing NiFe2O4 QDs as additive substitutes, the overall carbon content in cathodes is reduced to a minimal level of 5%, avoiding the excessive electrolyte consumption and guaranteeing specific energy parameters. To affirm such functionalities of NiFe2O4 QDs, we have deliberately evaluated cell performances in electrolyte solutions without extra addition of LiNO3. As confirmed, QDs-involved cathodes showcase a great specific capacity of 921.1 mAh g−1 at 0.2 A g−1, decent rate capability (remaining 526 mAh g−1 at 5 A g−1), and very impressive cyclic stability over 500 cycles (capacity decay rate: 0.08% per cycle at 0.2 A g−1; almost all Coulombic efficiencies beyond 96%). The concept of “building cathodes of Li–S cells with cost-effective, durable and versatile QDs” may arouse global research interest in designing well-fitted/compatible mixed metal oxide species and construction of low-carbon-content electrode for more practical Li–S cells.

2 Experimental Section

2.1 Preparation of NiFe2O4 QDs

Typically, ~1.62 g ferric chloride (purity > 99.99%, Sigma-Aldrich) and ~1.45 g nickel chloride (purity > 99.99%, Alfa) are dissolved into ~80 mL of deionized water with an ultrasonication treatment for 30 min. The resultant solution is magnetically stirred at ambient atmospheres and dripped with concentrated ammonia (Sigma-Aldrich) until the solution pH value reaches 8. After vigorously stirring for 10 min, the obtained mixture is transferred into a Teflon-lined stainless-steel autoclave and heated at 190 °C for 10 h. When cooled down to room temperature naturally, red powder samples are fetched out by centrifugation, washed with deionized water and ethanol several times, and dried at 60 °C for later use.

2.2 Preparation of S@CB ⊆ QDs Cathodes

S@CB ⊆ QDs hybrid samples are obtained by a heat treatment toward uniform powder mixtures containing ~8.5 g of sublimed S (Sigma-Aldrich), ~0.5 g carbon black (CB; Ketjenblack EC-300 J), and ~1 g of as-made NiFe2O4 QDs at 165 °C for 12 h. For cathode fabrication, such hybrid powders are carefully grinded, mixed with PVDF (Sigma-Aldrich) at a mass ratio of 9:1, and dispersed into moderate NMP (Fluka, 40 mg mL−1) to form homogeneous slurry. The calculated S ratio for S@CB ⊆ QDs cathodes is 76.5% in theory (if excluding the polymer binder mass, the theoretical S ratio should be ~85%). The slurry is then pasted onto an aluminum foil and dried at 60 °C for 10 h in a vacuum oven. For comparison study, the counterpart of S@CB hybrids is also prepared using the same procedures without the addition of NiFe2O4 QDs.

2.3 Materials Characterization and Electrochemical Testing

Fluorescent properties for QDs are measured by using a fluorescence spectrophotometer (FluoroMax-4, HORIBA, Japan). Phase structures of specimens are characterized by X-ray powder diffraction (XRD; D8 Advanced diffractometer with Cu Kα radiation, λ = 1.5418Å). The subtle geometric morphology and crystalline structure are detected
by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F) and transmission electron microscopy (HRTEM, JEM-2010F) equipped with energy-dispersive X-ray spectroscopy (EDS). In order to clarify the surface compositions, X-ray photoelectron spectroscopy (XPS; PerkinElmer model PHI 5600 spectrometer) is employed as well. The Raman spectra are recorded on a Renishaw 1000 NR Ar laser Raman spectroscope (532 nm laser) at ambient atmospheres. Thermogravimetric (TG; SDT600, USA) is also performed to determine the mass content under N₂ atmospheres. Tap density values for synthesized samples (S@CB ⊆ QDs, S@CB, NiFe₂O₄ QDs) are determined by a tapping tester (JF-20, Xiamen, China; vibration frequency: 250 tap min⁻¹; amplitude: 3 mm; total counter: 8000 times). Other tap density parameters for commercial CB (0.25 mg cm⁻²) and sublimed S powders (1.2 mg cm⁻²) are directly obtained from reagent suppliers. All 2032-type coin cells are assembled with a cathode (S@CB ⊆ QDs or S@CB), a Li foil anode, and a separator (Celgard 2300 membrane, purchased from Sigma-Aldrich) in an Ar-filled glovebox (Mikrouna Super; H₂O < 0.1 ppm, O₂ < 0.1 ppm). The electrolyte for Li–S cell testing is 1 M lithium bis-(trifluoromethanesulfonyl) imide dissolved in 1,3-dioxolane and dimethoxymethane (1:1 by volume) solvent. To clarify the actual S loading of tested electrodes (size: 12 mm), we have purposely measured the involved S content toward electrode specimens in the same batch. The actual S mass loading is eventually determined to be ~4.7 ± 0.1 mg per cell by a thermal treatment. The electrolyte/sulfur (E/S) ratio herein is measured to be a central value of ~4.26 μL mg⁻¹. On a CS310 electrochemical workstation, the cyclic voltammetry (CV) test is conducted between ~1.6 and ~2.8 V at a scan rate of ~0.1 mV s⁻¹, and the electrochemical impedance spectroscopy (EIS) measurements are carried out from 100 kHz to 0.1 Hz. Galvanostatic charge/discharge tests are conducted at varied current densities within a cutoff voltage window of 1.6–2.8 V using a professional battery tester (Land, China). To check the polysulfide adsorption ability, ~50 mg NiFe₂O₄ QDs are added into 5 mL ~0.3 mol L⁻¹ Li₂S₆ solution (pre-made by dissolving Li₂S and S with a molar ratio of 1:5 into dimethoxymethane under vigorously stirring at 80 °C).

3 Results and Discussions

3.1 Basic Morphological and Structural Characterization

The schematic illustration in Fig. 1 manifests the general working mechanism of NiFe₂O₄ QDs in cathodes for Li–S cells. Generally, current mainstream materials combined with S or Li₂S actives are still various bulky frameworks/matrix made up of hierarchically porous graphene, biomass-derived microporous carbons or high-specific-surface metallic organics. However, these S reservoir scaffolds are proven imperfect for actives loading due to (i) overmuch presence of spatial void places that are doomed to need flooded/excess electrolyte solution for complete electrode infiltration and (ii) lack of strong/polar binding interactions for anchoring dissociative molecules. In contrast, the ternary material NiFe₂O₄ itself has pronounced chemisorption/catalytic activities for soluble Li₂Sn intermediates, and meanwhile good electrical conductivity to compensate undesired intrinsically insulating properties of S-based actives. Moreover, its QDs form enables good organic electrolyte wettability and more exposed active spots on surface for polysulfide immobilization. In a crystalline structure of NiFe₂O₄ QDs, both Ni and Fe atoms can provide large quantities of chemisorption sites on surface edges to confine Li₂Sn molecules via electrostatic interactions, and meanwhile Ni constituents would improve Li₂S nucleation rate through strong-binding vacancy sites and catalytically accelerate their phase conversion. In particular, the smart use of NiFe₂O₄ QDs substitutes entails a fact that all involved carbon content in cathodes can be largely decreased to an extremely low level of 5%, thus forming more dense/compact electrodes rather than ones full of internal pores [24]. Practically, it is surprising to notice these functional NiFe₂O₄ QDs can evenly integrate with S@CB to form highly dispersive and individual units; thereby, S actives together with their derivatives yielded in charge/discharge processes would be firmly restricted nearby QDs or local positions inside cathode regions. Besides, aided by efficient electrochemical catalysis of NiFe₂O₄ QDs, the assembled Li–S cells can exhibit very stable cyclic behaviors even without the extra addition of LiNO₃ into the electrolyte solution, as discussed in later sections [25, 26].
Then, the structural information of NiFe$_2$O$_4$ QDs has been examined by FESEM and TEM (Fig. 2a–c). Basic top-view FESEM and TEM observations reveal fresh NiFe$_2$O$_4$ QDs are evenly dispersed in the absence of any aggregations. The statistical analysis on QDs (Fig. 2d) reflects that their mean diameter size is centralized at ~ 7.88 nm within a standard deviation of ~ 1.66 nm. The well-defined crystalline lattices with spacing distances of ~ 0.25 and ~ 0.29 nm successively correspond to the characteristic (311) and (220) lattice planes of cubic NiFe$_2$O$_4$ (JCPDS No. 74-2081). Figure 2e, f shows typical FESEM and EDS detections on ultimate S@CB ⊆ QDs samples to uncover their delicate geometric/inherent properties. We note that such foreign NiFe$_2$O$_4$ QDs have perfectly coalesced with S@CB nanoparticles to form individual hybrid nano units (average size: ~ 150 nm) instead of micro bulks. The EDS spectrum (inset in Fig. 2f) and mapping results (Fig. 2g–l) further affirm the homogenous elemental distribution of Ni, Fe, O, S, and C in specimens. Their TEM observations (Fig. S2a, b) clearly reveal that there evenly distribute plenty of NiFe$_2$O$_4$ QDs (size: ~ 10 nm) and CB nanoparticles (size: ~ 30 nm) surrounding the S matrix, confirming the successful hybrid construction of S@CB ⊆ QDs products (though close HRTEM observations toward interfaces between NiFe$_2$O$_4$ QDs and S are hardly achieved due to evident S sublimation under the high-energy electron beam condition, we successfully capture the significant information on robust NiFe$_2$O$_4$ QDs/CB interfaces and prominent adhesive capabilities for NiFe$_2$O$_4$ QDs; see Fig. S2c). The XRD pattern (Fig. S3) depicts the samples’ crystallographic phase at distinct evolution stages. Obviously, diffraction peaks detected at 28.4°, 34.8°, 42.5°, 53°, and 62.3° in both NiFe$_2$O$_4$ QDs and S@CB ⊆ QDs samples correspond well to (220), (311), (400), (422), (511), and (440) facets of cubic NiFe$_2$O$_4$ (JCPDS card No. 74-2081; space group: Fd-3m). After S infusion, intense peaks emerging at 21.1°, 22.3°, 25°, 25.9°, 27°, 27.9°, and 30.6° can be all indexed to monoclinic S (JCPDS card No. 74-2107; space group: P-21). The Raman peaks at ~ 143, ~ 202, ~ 289, ~ 548, and ~ 665 cm$^{-1}$ (Fig. S4) successively correspond to $T_{2g}^1(1)$, $E_g$, $T_{2g}^2(3)$ and $A_{1g}$ modes for cubic NiFe$_2$O$_4$, keeping in line with previous literature [27–29]. Peak signals at ~ 143 and ~ 202 cm$^{-1}$ ($T_{2g}^2(1)$ mode)
are mainly assigned to Fe–O vibrations due to the translational movement of tetrahedron atoms, while the ones at ~289 cm\(^{-1}\) (\(E_g\) mode) and ~548 cm\(^{-1}\) (\(T_{2g}\) (3) mode) result from symmetric bending of O with respect to Fe/Ni atoms and vibrations of octahedral groups. The symmetric stretching of Fe–O or Ni–O bonds in NiFe\(_2\)O\(_4\) would also lead to a Raman peak at ~665 cm\(^{-1}\) (\(A_{1g}\) mode). The additional visible peak at a wavenumber of ~464 cm\(^{-1}\) comes from the elemental S, and other two strong peaks at ~1346 and ~1585 cm\(^{-1}\) are ascribed to fingerprint D and G bands for CB, respectively. Besides, the TG measurement (Fig. S5) declares the total S weight percentage is up to ~75 wt% in S@CB \(\subseteq\) QDs.

The physical density of commercial CB, sublimed S, S@CB \(\subseteq\) QDs, and pure NiFe\(_2\)O\(_4\) QDs is visually compared, as presented by a photograph in Fig. 3a. All sample powders are pre-tapped for efficient materials packing. Also, their key parameters of tap density and specific surface areas are successively plotted in Fig. 3b, c. The tap density value of CB is as low as ~0.25 g cm\(^{-3}\), over four times less than S (~1.26 g cm\(^{-3}\)) and NiFe\(_2\)O\(_4\) QDs (~1.43 g cm\(^{-3}\)). By contrast, the specific surface area of CB even reaches a value of ~800 cm\(^2\) g\(^{-1}\) (the standard is given by CB suppliers), far higher than that of either NiFe\(_2\)O\(_4\) QDs (~80.8 cm\(^2\) g\(^{-1}\)) or S (~9.3 cm\(^2\) g\(^{-1}\)). Consequently, excessive use of sparse carbons is doomed to consume overmuch electrolytes to infiltrate all interior surfaces in cathodes, augmenting cells weight and lowering their specific energy. To make dense cathodes with minimized electrolyte uptake, practical S hosts are ought to own proper surface areas (<100 m\(^2\) g\(^{-1}\)) and tap density (0.7–1 g cm\(^{-3}\)), as declared in recent literature [11]. By employing NiFe\(_2\)O\(_4\) QDs as additive substitutes, the as-formed S@CB \(\subseteq\) QDs possess more appropriate tap density (~1.32 g cm\(^{-3}\)) and specific surface area (~19.9 m\(^2\) g\(^{-1}\)) values than S@CB counterparts, holing great potential in Li–S cell applications.
3.2 Electrochemical Testing and Analysis

The catalytic effects of NiFe$_2$O$_4$ QDs for polysulfide conversion kinetics are primarily probed by cyclic voltammetry (CV) method in a voltage window of −0.5 to 0.5 V for Li$_2$S$_6$ symmetric cells. To exclude irrelevant influences, we also intentionally plot the CV curve of S@CB for a clear comparison study (Fig. 4a). S@CB ⊆ QDs electrodes exhibit far higher CV response than S@CB, confirming their superior electrochemically catalytic behaviors [30, 31]. This should be associated with a unique phenomenon that electropositive Fe atoms at corner sites (Fig. 1) tend to leach out by polysulfide etching, leaving rich vacant defects around Ni sites and hence facilitating/activating redox reactions [32].

An visualized adsorption experiment is further performed by adding NiFe$_2$O$_4$ QDs into a Li$_2$S$_6$ solution (∼0.3 mol L$^{-1}$) to testify their absorption ability (Fig. 5b). Compared to pure concentrated Li$_2$S$_6$ solution, NiFe$_2$O$_4$ QDs-contained liquid becomes colorless after few hours, solidly certifying the excellent chemisorption capability of QDs toward Li$_2$S$_n$. To better confirm practical functions of NiFe$_2$O$_4$ QDs in full-cell operation, we have purposely excluded positive effects/contributions (e.g., on Li$_2$Sn shuttling suppression) from additive salts and executed all cell measurements in LiNO$_3$-free electrolytes. Figure 4c shows CV curves of S@CB ⊆ QDs cathodes between 1.6 and 2.8 V (vs. Li/Li$^+$) at a scanning rate of 0.1 mV s$^{-1}$ for initial five cycles. Cathodic peaks at ~2.38 and ~2.1 V are ascribed to the electrochemical transformation of S$_8$ into long-chain polysulfide species and further reductions into solid Li$_2$S$_2$/Li$_2$S, respectively. In subsequent anodic scans, the overlapped anodic peaks at ~2.58 V result from reverse complex oxidation reactions from Li$_2$S$_n$ ($n = 1 - 2/4 - 8$) to pristine S$_8$ [33–35]. With regard to S@CB cathodes (Fig. S6), there are similar cathodic/anodic peaks but obvious potential polarization/sluggish phenomena accompanied in early cyclic periods. The onset potential positions for characteristic redox peaks of S@CB ⊆ QDs and S@CB are also labeled, respectively (see CV plots in Fig. S6). The anodic peak of S@CB ⊆ QDs is initiated at ~2.39 V, whereas the two-step cathodic peaks are successively lying at ~2.51 V (corresponding to S$_8$ transformation into long-chain Li$_2$S$_n$ (n ≥ 4)) and ~2.17 V (indexed to changes from low-order Li$_2$S$_n$ (n < 4) to Li$_2$S). Compared to S@CB cases with a higher anodic peak position of ~2.43 V and lower cathodic ones at ~2.46 and ~2.16 V, NiFe$_2$O$_4$ QDs-involved electrodes demonstrate upper electrochemical activities and lowered energy barriers for the onset of redox peaks. Such enhanced redox reaction kinetics are closely associated with intrinsic positive effects deriving from NiFe$_2$O$_4$ QDs, which can electrocatalytically push forward electrochemical conversions of S-based active species.

Galvanostatic charge–discharge curves of S@CB ⊆ QDs under 0.1 A g$^{-1}$ at the 1st, 50th, 100th, 300th, and 500th cycle (Fig. S7) reveal two distinct plateaus appear at ~2.38 and ~2.1 V, which are in accordance to classic multi-step reductions of S$_8$. The presence of a long and flat plateau at ~2.58 V agrees well with our former CV analysis. Even after 500 times of deep cycling, the well-defined presence of such characteristic voltage plateaus affirms the durable redox kinetics and cyclic performance of S@CB ⊆ QDs. Figure 4d shows the long cyclic records of S@CB and S@CB ⊆ QDs at 0.2 A g$^{-1}$. S@CB ⊆ QDs hybrids can deliver a remarkable discharge capacity of ~910 mAh g$^{-1}$ and inappreciable
Fig. 4  a CV curve comparisons between QDs-involved and QDs-free cathodes. b Adsorption ability of NiFe₂O₄ QDs in Li₂S₆ electrolyte. Electrochemical testing results on S@CB ⊆ QDs: c CV curves, d long-term cyclic performance, e rate-varied cyclic record and f rate-varied voltage profiles.

Fig. 5  Comparison analysis of S@CB ⊆ QDs before and after 500 cycles via techniques of a XRD, b SEM, c EIS and d-f XPS: d S 2p, e Fe 2p₃/₂, and f Ni 2p₃/₂
capacity fading (only ~0.09% per cycle) even after 500 cycles with all Columbic efficiencies over 96%. In sharp contrast, after limited 100 cycles, S@CB cathodes exhibit only ~43.8% of initial capacity (~908 mAh g⁻¹), along with very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode diameter is 12 mm (electrode area: ~1.13 cm²), the areal values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%). Given the cathode very fluctuant/unsteady Columbic efficiency records (values jumping between 82% and 109%).

Figure S9 shows the EIS testing results fitted by the inset Randles equivalent circuit. $R_1$ in the circuit model represents the bulky resistance caused by the electrolyte phase as well as other parts of cell configurations, corresponding to the intercept with the real axis at a high-frequency range. There is no large difference in $R_1$ between these two electrodes; the $R_1$ value (~1.58 Ω) of S@CB is a bit lower than that of S@CB ⊆ QDs (~4.89 Ω), which may be induced by the increment of local electrolyte absorption/concentration for carbon-rich cathodes. $R_2$ and $CPE_1$ successively represent the charge-transfer resistance and related capacitance reflecting the kinetic nature at the solid/electrolyte interface. S@CB ⊆ QDs electrodes own a smaller $R_2$ value (~114.8 Ω) than S@CB counterparts (~159.7 Ω), suggesting their upper physicochemical properties aided by the addition of NiFe₂O₄ QDs. $W_1$ refers to the diffusion impedance correlating with Li⁺ diffusion processes through a bulk cathode, as reflected by a tail-like slope at the low-frequency range [25, 36]. A larger slope of S@CB ⊆ QDs electrode indicates their superior mass-transfer behaviors for Li⁺. The corresponding Li⁺ diffusion coefficient ($D_{Li⁺}$) and double layer capacitance ($C_d$) can be calculated according to formulas below:

$$D_{Li⁺} = \frac{R^2T^2}{2A^2n^4F^4c^4\sigma^2}$$

$$C_d = \frac{1}{R_{ct}}$$

where $R$ refers to the gas constant (8.3143 J K⁻¹ mol⁻¹), $T$ is the absolute temperature, $A$ is the area of electrode, $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant, $C_{Li⁺}$ is the Li⁺ concentration, $\sigma$ is the Warburg factor, and $\omega$ is the angular velocity. Figure S10 reflects the S@CB ⊆ QDs cathode even possesses a higher $D_{Li⁺}$ (4.14×10⁻⁸ cm² s⁻¹) than S@CB (0.52×10⁻⁸ cm² s⁻¹), which is possibly associated with shortened Li⁺ diffusion paths or surface ion diffusivity due to less carbon usage [37]. Moreover, the $C_d$ of S@CB ⊆ QDs cathode (7.3×10⁻⁷ F) is far lower than that of S@CB (1.74×10⁻⁶ F), mainly attributing to diminished specific areas of S@CB ⊆ QDs. The rate performance (Fig. 4e) is also estimated at different current rates from 0.2 to 5 A g⁻¹. Apparently, the average discharge capacity of S@CB ⊆ QDs electrodes slightly drops from 910 to 691, 636, 589, and 526 mAh g⁻¹ when the current rate stepwise increases from 0.2 to 1, 2, 3, and 5 A g⁻¹, whose records are much better than those of S@CB (901, 352, 287, 226, and 153 mAh g⁻¹). Figure 4f displays typical voltage profiles of S@CB ⊆ QDs. Specifically, S@CB ⊆ QDs cathodes exhibit relatively lower potential polarization ($\Delta V = 140$ mV) when compared to S@CB cases ($\Delta V = 365$ mV; Fig. S11), declaring effectively improved cell kinetics due to the addition of NiFe₂O₄ QDs. To further make clear effects induced by S loading ratio, basic electrochemical behaviors of cathodes with ramped S areal mass densities (including 4, 8, 10, and 12 mg cm⁻²) have been provided for comparative study (Fig. S12). Similar to the former case (~754 mAh g⁻¹) under an areal mass of ~4 mg cm⁻², S@CB ⊆ QDs cathodes (at ~8 mg cm⁻²) can maintain a comparable reversible capacity of ~702 mAh g⁻¹. However, when S loading rises to a level of 10 or 12 mg cm⁻², the evident capacity degradations of S@CB ⊆ QDs cathodes are noticed (Fig. S12a), with delivered specific capacities of ~465 and ~266 mAh g⁻¹, respectively. (Corresponding specific capacity vs. mass loading plot is displayed in Fig. S12b.) This is mainly attributed to a fact that such a highly thicken/compact electrode film is not beneficial for electrolytic infiltration, leading to reduced active utilization and deteriorated electrode operation stability (see Coulombic efficiency record in Fig. S12c; especially when S areal mass increases to 12 mg cm⁻², huge fluctuations on Coulombic efficiency values are rather distinct).

### 3.3 Postmortem Analysis on Cycled Cathodes

Postmortem analysis on cycled cathodes is systematically conducted as well. Figure 5a shows the XRD pattern of S@CB ⊆ QDs after 500 cycles. All detectable diffraction peaks accord well with those belonging to NiFe₂O₄ QDs, except for a broad bump-like diffraction peak at ~23.3° stemming from electrolytic residuals; no other possible substances (e.g., FeS, FeOₓ, NiS, and NiO) are probed,
confirming the outstanding electrochemical stability of NiFe₂O₄ QDs. The geometrical morphology of fatigue S@CB ⊆ QDs cathodes (Fig. 5b) clearly reveals the absence of any flower-like S crystals formation. Elemental mapping records (Fig. S13) further evidence the same uniform distribution of Ni, Fe, O element as before. The EIS testing toward S@CB ⊆ QDs cathodes before and after 500 cycles have been compared (Fig. 5c). The $R_2$ for cycled S@CB ⊆ QDs electrodes (~ 40.3 Ω) is far lower than the value of fresh ones (~ 114.4 Ω), which might be due to remarkable reconfiguration/rearrangement of S actives in cathode regions among repeated charge/discharge processes. A higher slope suggests Li⁺ transfer rate is also enhanced due to the setup of electrochemical reaction equilibrium preferable for redox conversion. Their surface chemistry and composition are further analyzed by XPS (Fig. 5d–f). The pristine S 2p spectrum exhibits a typical spin–orbit doublet at ~ 162.7 (S 2p₃/₂) and ~ 164.1 eV (S 2p₁/₂), successively attributing to the terminal and bridging S (Fig. 5d) [38]. The additional peak situated at ~ 167.6 eV refers to sulfate species resulted from oxidation during sample synthesis. In contrast, great changes in S 2p spectrum have been observed for cycled electrodes owing to the presence of intensified peak centralized at ~ 167.3 eV, which is mostly responsible for the formation of metal (Fe or Ni)-S bonds via dangling bonds on NiFe₂O₄ QDs [39]. Inherent interaction protocols aforementioned are also validated by Fe 2p₃/₂ and Ni 2p₃/₂ spectra. Figure 5d compares the Fe 2p₃/₂ spectrum of S@CB ⊆ QDs cathode before and after cycling. The initial Fe 2p₃/₂ core-level spectrum (Fig. 5e) exhibits a characteristic peak (~ 710.4 eV) as well as one shake-up satellite peak (~ 719.1 eV), indicative of a typical Fe²⁺ (Fe–O bond) chemical state. After cycling, there is a novel peak arising at a lower position of ~ 705.1 eV, which is assigned to a chemical condition of Fe³⁺ (Fe–S bond). Similarly, the Ni 2p₃/₂ XPS spectrum (Fig. 5f) of cycled cathodes also shows a new peak redshifted to ~ 853.2 eV, which can be elucidated by the formation of Ni-S bond. Given the absence of crystalline phase changes on NiFe₂O₄ QDs judged by previous XRD analysis, we conclude that strong chemical interactions between NiFe₂O₄ QDs and polysulfides should be the most convincing reason to account for above results [40–43].

4 Conclusions

In summary, low-cost and multi-functionalized NiFe₂O₄ QDs with exceptional electrolyte wettability, rich surface adsorption/catalytic sites, and good electrical conductivity have been used as additive substitutes to curtail the carbon usage and hence build more practical S cathodes for Li–S cells. The carbon content can be greatly decreased from ~26% (a mean percentage level in S/C hybrids) to a low value of ~5% for our S@CB ⊆ QDs. We also affirm NiFe₂O₄ QDs additives own excellent chemisorption interactions with soluble polysulfide molecules and prominent catalytic properties for Li₂Sₙ phase conversions and meantime boost the charge-transfer capability/redox kinetics of entire cathode systems. As a consequence, the designed S@CB ⊆ QDs hybrid cathodes demonstrate outstanding rate behaviors and quite stable cyclic performance in LiNO₃-free electrolytes (only ~0.08% capacity fade per cycle in 500 cycles at 0.2 A g⁻¹; Coulombic efficiency stays above 96%). Our present work may have great potential for the rational design of low-carbon-content electrodes and meanwhile arise tremendous research interest in exploiting more optional/useful QDs additives for practical Li–S cell systems.

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References

1. J. Cheng, J. Shang, Y.M. Sun, L.K. Ono, D.R. Wang et al., Flexible and stable high-energy lithium-sulfur full batteries with only 100% oversized lithium. Nat. Commun. 9, 4480 (2018). https://doi.org/10.1038/s41467-018-06879-7

2. Z.L. Xu, S.H. Lin, N. Onofrio, L.M. Zhou, F.Y. Shi, W. Lu, K. Kang, Q. Zhang, S.P. Lau, Exceptional catalytic effects of black phosphorus quantum dots in shutting-free lithium sulfur batteries. Nat. Commun. 9, 4164 (2018). https://doi.org/10.1038/s41467-018-06629-9

3. L.L. Fan, M. Li, X.F. Li, W. Xiao, Z.W. Chen, J. Lu, Interlayer material selection for Lithium-Sulfur batteries. Joule 3, 361–386 (2019). https://doi.org/10.1016/j.joule.2019.01.003

4. J. Pu, Z.H. Shen, J.X. Zheng, W.L. Wu, C. Zhu et al., Multifunctional Co3S4@sulfur nanotubes for enhanced Lithium-Sulfur battery performance. Nano Energy 37, 7–14 (2017). https://doi.org/10.1016/j.nanoen.2017.05.009

5. Z.H. Li, Q. He, X. Xu, Y. Zhao, X.W. Liu et al., A 3D nitrogen-doped graphene/TiN nanowires composite as a strong polysulfides anchor for lithium-sulfur batteries with enhanced rate performance and high areal capacity. Adv. Energy Mater. 30, 1804089 (2018). https://doi.org/10.1002/aenm.201804089

6. S. Choi, C. Kim, J.M. Suh, H.W. Jang, Reduced graphene oxide-based materials for electrochemical energy conversion reactions. Carbon Energy 1, 85–108 (2019). https://doi.org/10.1002/cenm.201701110

7. Y. Zhong, X.H. Xia, S.J. Deng, J.Y. Zhan, R.Y. Fang et al., Popcorn inspired porous macroellular carbon: rapid puffing fabrication from rice and its applications in lithium-sulfur batteries. Adv. Energy Mater. 8, 1701110 (2017). https://doi.org/10.1002/aenm.201701110

8. Y.Y. Shi, G.J. Liu, R.C. Jin, H. Xu, Q.Y. Wang, S.M. Gao, Carbon materials from melamine sponges for supercapacitors and lithium battery electrode materials: a review. Carbon Energy 1, 253–275 (2019). https://doi.org/10.1002/cenm.201701110

9. F. Liu, C.J. Wang, X. Sui, M.A. Riaz, M.Y. Xu, L. Wei, Y. Chen, Synthesis of graphene materials by electrochemical exfoliation: recent progress and future potential. Carbon Energy 1, 173–199 (2019). https://doi.org/10.1002/cenm.201701110

10. Q. Wu, L.J. Yang, X.Z. Wang, Z. Hu, From carbon-based nanotubes to nanocages for advanced energy conversion and storage. Acc. Chem. Res. 50, 435–444 (2017). https://doi.org/10.1021/acs.accounts.6b00541

11. A. Bhargav, J.R. He, A. Gupta, A. Manthiram, Lithium-sulfur batteries: attaining the critical metrics. Joule 4, 1–6 (2020). https://doi.org/10.1016/j.joule.2020.01.001

12. S.H. Chung, C.H. Chang, A. Manthiram, Progress on the critical parameters for lithium-sulfur batteries to be practically viable. Adv. Funct. Mater. 28, 1801188 (2018). https://doi.org/10.1002/adfm.201801188

13. M.J. Klein, G.M. Veith, A. Manthiram, Rational design of lithium-sulfur battery cathodes based on experimentally determined maximum active material thickness. J. Am. Chem. Soc. 139, 9229–9237 (2017). https://doi.org/10.1021/jacs.7b03380

14. J.J. Park, J.H. Moon, C.J. Kim, J.H. Kang, E. Lim et al., Graphene quantum dots: structural integrity and oxygen functional groups for high sulfur/sulfide utilization in lithium sulfur batteries. NPG Asia Mater. 8, e272 (2016). https://doi.org/10.1038/am.2016.61

15. X.Y. Tao, J.G. Wang, Z.J. Ying, Q.X. Cai, G.Y. Zheng et al., Strong sulfur binding with conducting magnéli-phase TiO2n–1 nanomaterials for improving lithium-sulfur batteries. Nano Lett. 14, 5288–5294 (2014). https://doi.org/10.1021/nl502331f

16. X. Liang, C. Hart, Q. Pang, A. Garsuch, T. Weiss, L.F. Nazar, A highly efficient polysulfide mediator for lithium-sulfur batteries. Nat. Commun. 6, 5682 (2015). https://doi.org/10.1038/ncomms6682

17. S.S. Zhang, D.T. Tran, Pyrite FeS2 as an efficient adsorbent of lithium polysulphide for improved lithium-sulfur batteries. J. Mater. Chem. A 4, 4371–4374 (2016). https://doi.org/10.1039/C6TA01214K

18. M. Nawwar, R. Poon, R. Chen, R.P. Sahu, I.K. Puri, I. Zhiltomisky, High areal capacitance of Fe3O4-decorated carbon nanotubes for supercapacitor electrodes. Carbon Energy 1, 124–133 (2019). https://doi.org/10.1002/cenm.201701110

19. X. Liu, J.Q. Huang, Q. Zhang, L.Q. Mai, Nanostructured metal oxides and sulfides for lithium-sulfur batteries. Adv. Mater. 29, 1601759 (2017). https://doi.org/10.1002/adma.201601759

20. X. Liang, C.Y. Kwok, F. Lodi-Marzano, Q. Pang, M. Cuisinier et al., Tuning transition metal oxide-sulfur interactions for long life lithium sulfur batteries: the “Goldilocks” principle. Adv. Energy Mater. 6, 1501636 (2016). https://doi.org/10.1002/aenm.201501636

21. Y. Lu, X.N. Li, J.W. Liang, H. Lei, Y.C. Zhu, Y.T. Qian, A simple melting-diffusing-reacting strategy to fabricate S/NiS2-C for lithium-sulfur batteries. Nanoscale 8, 17616–17622 (2016). https://doi.org/10.1039/c6nr05626a

22. Y. Li, J. Chen, Y.F. Zhang, Z.Y. Yu, T.Z. Zhang, W.Q. Ge, L.P. Zhang, NiS/rGO/S capable of lithium polysulfide trapping as an enhanced cathode material for lithium sulfur batteries. J. Alloy. Compd. 766, 804–812 (2018). https://doi.org/10.1016/j.jallcom.2018.06.369

23. Q. Fan, W. Liu, Z. Weng, Y.M. Sun, H.L. Wang. Ternary hybrid material for high-performance lithium-sulfur battery. J. Am. Chem. Soc. 137, 12946–12953 (2015). https://doi.org/10.1021/jacs.5b07071

24. X.T. Gao, Y. Xie, X.D. Zhu, K.N. Sun, L.F. Nazar, Ultrathin MXene nanosheets decorated with TiO2 quantum dots as an efficient sulfur host toward fast and stable Li-S batteries. Small 14, 1802443 (2018). https://doi.org/10.1002/smll.201802443

25. Y. Hu, W. Chen, T.Y. Lei, B. Zhou, Y. Jiao et al., Carbon quantum dots-modified interfacial interactions and ion conductivity for enhanced high current density performance in Lithium-Sulfur batteries. Adv. Energy Mater. 9, 1802955 (2018). https://doi.org/10.1002/aenm.201802955

26. R.P. Fang, S.Y. Zhao, S.F. Pei, X.T. Qian, P.X. Hou, H.M. Zhang,  NiS2/rGO/S capable of lithium polysulfide trapping as an all-graphene cathode structure. ACS Nano 10, 8682–8686 (2016). https://doi.org/10.1021/acsnano.6b04019
27. A.J. Ahlawat, V.G. Sathe, V.R. Reddy, A.M. Gupta, Raman and X-ray diffraction studies of superparamagnetic NiFe\(_2\)O\(_4\) nanoparticles prepared by sol-gel auto-combustion method. J. Magn. Magn. Mater. 323, 2049–2054 (2011). https://doi.org/10.1016/j.jmmm.2011.03.017

28. A.J. Ahlawat, V.G. Sathe, Raman study of NiFe\(_2\)O\(_4\) nanoparticles, bulk and films: effect of laser power. J. Raman Spectrosc. 42, 1087–1094 (2011). https://doi.org/10.1002/jrs.2791

29. S. Deng, Y. Zhong, Y. Zeng, Y. Wang, X. Wang et al., Hollow TiO\(_2@\)Co\(_9\)S\(_8\) core-branch arrays as bifunctional electrocatalysts for efficient oxygen/hydrogen production. Adv. Sci. 5, 1700772 (2018). https://doi.org/10.1002/advs.201700772

30. Y. Wang, R. Zhang, Y.C. Pang, X. Chen, J. Lang et al., Carbon@Titanium nitride dual shell nanospheres as multifunctional hosts for lithium sulfur batteries. Energy Storage Mater. 16, 228–235 (2019). https://doi.org/10.1016/j.ensm.2018.05.019

31. L. Zhang, Z. Chen, F.N. Dong, M. Li, C. Diao et al., Nickel-cobalt double hydroxide as a multifunctional mediator for ultrahigh-rate and ultralong-life Li-S batteries. Adv. Energy Mater. 8, 1802431 (2018). https://doi.org/10.1002/aenm.201802431

32. X.D. Jia, Y.F. Zhao, G.B. Chen, L. Shang, R. Shi et al., Water splitting: Ni,FeN nanoparticles derived from ultrathin NiFe-layered double hydroxide nanosheets: an efficient overall water splitting electrocatalyst. Adv. Energy Mater. 6, 1502585 (2016). https://doi.org/10.1002/aenm.201502585

33. J. Xu, W. Zhang, H. Fan, F. Cheng, D. Su, G. Wang, Promoting lithium polysulfides/sulfide redox kinetics by the catalyzing of zinc sulfide for high performance Lithium-Sulfur battery. Nano Energy 51, 73–82 (2018). https://doi.org/10.1016/j.nanoen.2018.06.046

34. K. Xi, D. He, C. Harris, Y. Wang, C. Lai et al., Enhanced sulfur transformation by multifunctional FeS\(_2@\)Fe/S composites for high-volumetric capacity cathodes in Lithium-Sulfur batteries. Adv. Sci. 6, 1800815 (2019). https://doi.org/10.1002/advs.201800815

35. L.Y. Hu, C.L. Dai, H. Liu, Y. Li, B.L. Shen et al., Doubleshelled NiO-NiCo\(_2\)O\(_4\) heterostructure@carbon hollow nanocages as an efficient sulfur host for advanced lithium-sulfur batteries. Adv. Energy Mater. 8, 1800709 (2018). https://doi.org/10.1002/aenm.201800709

36. Z.F. Deng, Z.A. Zhan, Y.Q. Lai, J. Liu, J. Li, Y.X. Liu, Electrochemical impedance spectroscopy study of a lithium/sulfur battery: modeling and analysis of capacity fading. J. Electrochem. Soc. 160, A553–A558 (2013). https://doi.org/10.1149/2.02630jes

37. W.W. Zeng, L. Wang, X. Peng, T.F. Liu, Y.Y. Jiang et al., Enhanced ion conductivity in conducting polymer binder for high-performance silicon anodes in advanced lithium-ion batteries. Adv. Energy Mater. 8, 1702314 (2018). https://doi.org/10.1002/aenm.201702314

38. H.J. Peng, Z.W. Zhang, J.Q. Huang, G. Xie, J. Zhang et al., A cooperative interface for highly efficient lithium-sulfur batteries. Adv. Mater. 28, 9551–9558 (2016). https://doi.org/10.1002/adma.201603401

39. M. Zhao, H.J. Peng, Z.W. Zhang, B.Q. Li, X. Chen et al., Activating inert metallic compounds for high-rate lithium-sulfur batteries through in situ etching of extrinsic metal. Angew. Chem. Int. Ed. 58, 3779–3783 (2019). https://doi.org/10.1002/anie.201812062

40. G.E. LeCroy, S.K. Sonkar, F. Yang, L.M. Veca, P. Wang et al., Toward structurally defined carbon dots as ultracompact fluorescent probes. ACS Nano 8, 4522–4529 (2014). https://doi.org/10.1021/nn406628s

41. Y. Hu, M.M. Awak, F. Yang, S.J. Yan, Q.W. Xiong et al., Photoexcited state properties of carbon dots from thermally induced functionalization of carbon nanoparticles. J. Mater. Chem. C 4, 10554–10561 (2016). https://doi.org/10.1021/nn406628s

42. W.L. Wu, J. Pu, J. Wang, Z.H. Shen, H.Y. Tang et al., Bioimimetic bipolar microcapsules derived from staphylococcus aureus for enhanced properties of lithium-sulfur battery cathodes. Adv. Energy Mater. 8, 1702373 (2018). https://doi.org/10.1002/aenm.201702373

43. T. Liu, C.J. Jiang, B. Cheng, W. You, J.G. Yu, Hierarchical Ni/S/N-doped carbon composite hollow spheres with excellent supercapacitor performance. J. Mater. Chem. A 5, 21257–21265 (2017). https://doi.org/10.1039/C7TA06149H