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# Metal/nanocarbon layer current collectors enhanced energy efficiency in lithium-sulfur batteries

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#### ABSTRACT

Lithium-sulfur (Li-S) batteries with intrinsic merits in high theoretical energy density are the most promising candidate as the next-generation power sources. The strategy to achieve a high utilization of active materials with high energy efficiency is strongly requested for practical applications with less energy loss during repeated cycling. In this contribution, a metal/nanocarbon layer current collector is proposed to enhance the redox reactions of polysulfides in a working Li-S cell. Such a concept is demonstrated by coating graphene–carbon nanotube hybrids (GNHs) on routine aluminum (Al) foil current collectors. The interfacial conductivity and adhesion between the current collector and active material are significantly enhanced. Such novel cell configuration with metal/nanocarbon layer current collectors affords abundant Li ions for rapid redox reactions with small overpotential. Consequently, the Li-S cells with nanostructured current collectors exhibit an initial discharge capacity of 1,113 mAh g<sup>-1</sup> at 0.5 C, which is ~300 mAh g<sup>-1</sup> higher than those without a GNH coating layer. The capacity retention is 73% for cells with GNH after 300 cycles. A reduced voltage hysteresis and a high energy efficiency of ca. 90% are therefore achieved. Moreover, the Al/GNH layer current collectors are easily implanted into current cell assembly process for energy storage devices based on complex multi-electron redox reactions (e.g., Li-S batteries, Li-O<sub>2</sub> batteries, fuel cells, and flow batteries).

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## 1. Introduction

Lithium-sulfur (Li-S) batteries attract huge attention as typical next-generation rechargeable batteries with intrinsic merits in high theoretical energy density, abundant and low-cost active materials of sulfur, and environmental benignity [1–4]. The electrochemical conversion reactions between sulfur and lithium render Li-S batteries with an ultrahigh theoretical energy density of 2,600 Wh kg<sup>-1</sup> (3–5 times those of routine lithium-ion batteries) [3–5]. However, the Li-S couple also brings complex multielectron redox conversions in a working cell [6–9].

The reduction of sulfur cathode undergoes a typical two-step process: (1) sulfur is reduced to high-order soluble polysulfides,  $Li_2S_x$  ( $4 \le x \le 8$ ); (2) high-order polysulfides are further reduced to  $Li_2S/Li_2S_2$  deposits [10–12]. These multi-electron redox reactions require abundant electrons and ions through robust electron pathways and interconnected ion channels, respectively, in a working

cell. However, the sulfur cathode is intrinsic insulate. During the past decades, numerous efforts have been devoted to develop various building blocks for sulfur accommodation in cathodes. Carbonaceous materials (e.g., carbon nanotubes (CNTs) [13,14], graphene [15–18], porous carbon [19–21], and their hybrids [22]) are widely used to form composites with sulfur materials to afford conducting networks towards high sulfur utilization. With the rational design of the porous structure of nanocarbon (e.g., microporous carbon [23,24], mesoporous carbon [25], and hollow carbon spheres [26]), sulfur materials can be hosted into micro/mesopores or hollow structures to partly limit the dissolution of polysulfide intermediates [27,28]. As the concept of chemical adsorption emerges, polar hosts (e.g., heteroatom doped carbon [29], metal oxides [30], metal sulfides [31], metal carbides [32], etc.) are introduced to retard the dissolution and diffusion of polysulfides through the tunable polar-polar interaction, metal-sulfur bond, or polysulfide catenation. Recently, electrocatalysts for sulfur redox reactions have also been incorporated into sulfur cathodes to propel the reaction kinetics of polysulfides, as well as to mitigate the loss of active materials [33–35].

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Beyond the rational design of sulfur composite units, emerging strategies are also proposed to efficiently host the composites at an electrode level. Recently, three-dimensional (3D) free-standing paper has been widely reported as either integrated electrodes or current collector scaffolds for sulfur cathodes [36]. Macroscopic porous assemblies of CNTs [37], carbon nanofibers [38], as well as 3D carbon/metal foams [39,40] are applied to accommodate sulfur composites with high loading amounts. However, 3D electrodes/current collectors are hardly compatible with current electrode fabrication procedures. The practical difficulties in electrode tab welding hinder the practical applications of 3D electrodes in high-capacity pouch cells.

Among the current materials processing for sulfur cathode fabrication, the slurry coating of sulfur composites onto aluminum (Al) foil current collectors remains the most compatible and operable process for bulk productions of Li-S batteries. The rise of sulfur loading in a working electrode is essential to meet the demand for a cell energy density that is practically acceptable [41,42]. However, both the electrical and mechanical contact deteriorate at the complex interfaces between electrode materials and the current collectors at a high sulfur loading. Such interfaces, as one of the major reasons for cell failure, remain a challenge. The interfaces between the Al foil and electrode materials are unstable due to the corrosion of Al foil and weak adhesion through the routine coating process [43]. These complex interfaces become even more intractable to deal with because of the insulating nature and huge volume change of composite cathodes during continuous operation of Li-S batteries. If the interfaces between the current collectors and electrode materials can be effectively regulated, the sulfur cathode can be used in an efficient and effective way, which is very crucial to boost the development of high-energydensity batteries.

The Al foil current collector is usually very rigid, which afford limited contacts and weak interaction with the electrode (Fig. 1a). If a nanocarbon layer can be introduced between Al foil and sulfur electrode, the contact between composite cathode and current collectors is expected to be significantly enhanced. Such robust interfaces can render a Li-S cell with high energy density and long cycle life. Based on this consideration, we incorporated a graphene-CNT hybrid (GNH) coating layer onto the Al foil to construct an artificial interface between the current collector and electrode materials (Fig. 1b). The GNH materials are highly conductive and mechanically stable. The hybrid structure also renders GNH materials self-dispersible properties to maintain the highly porous structures. The working Li-S cells with artificial interfaces between the Al foil and the electrode layers demonstrate not only high sulfur utilization and long cycling life, but also unexpected low overpotential for rapid redox reaction of polysulfides and high energy efficiency of a Li-S battery.

#### 2. Experimental

## 2.1. Fabrication of Al/nanocarbon layer current collector

The GNHs were fabricated by facile chemical vapor deposition (CVD) with the FeMgAl layered double hydroxides (LDHs) as catalyst precursor, as previously reported by our group [44]. Typically, the FeMgAl LDHs were prepared using a facile urea-assisted coprecipitation reaction with Fe(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O. The molar ratio of Fe:Mg:Al is 1:6:2. The FeMgAl LDHs were fed into a fluidized bed reactor for the CVD growth of GNHs at 950 °C with methane as carbon source (0.15 g min<sup>-1</sup>) and argon as carrying gas. Subsequently, the FeMgAl catalyst was removed by chemical treatment and deionized water washing to obtain high purity GNHs sample (99.5 wt%).



**Fig. 1.** (Color online) Schematic of the GNH coating layer as an artificial interface between the Al foil and sulfur cathodes.

To obtain Al/nanocarbon layer current collector, GNHs were firstly dispersed in a planetary mixer with poly(vinyl pyrrolidone) (PVP) and water to form uniform aqueous nanocarbon slurry. The mass ratio of GNH:PVP was 9:1. The aqueous GNH slurry was then facilely coated onto a continuous roll of Al foil with a width of 10 cm. The areal loading of composite layer was controlled to be 0.20 mg cm<sup>-2</sup>.

## 2.2. Fabrication of sulfur cathodes

Sulfur powder was purchased from Alfa Aesar with a high purity of >99.9% and used without further purification. CNTs, as conducting agents, were mixed with sulfur powder in a mass ratio of 3:7 by shaker-milling. The mixture subsequently underwent a heating process at 155 °C for 4 h to incorporate sulfur into the CNT matrix. The obtained CNT/S powder was milled with poly (vinylidene fluoride) binder in a mass ratio of 9:1 using *N*-methyl pyrrolidone (NMP) as the solvent to form cathode slurry. Asobtained slurry was coated onto the Al foil with or without a GNH layer by doctor blading and dried at 60 °C for 24 h. For coin cells, the sulfur content was 63% and the areal sulfur loading was set to 1.1 and 2.6 mg cm<sup>-2</sup>. In case of pouch cell evaluation, the areal sulfur loading amount was increased to 7.2 mg cm<sup>-2</sup>.

#### 2.3. Electrochemical measurements

Standard 2025 coin cells were employed to evaluate the electrochemical performance. The electrodes were punched into 13-mmdiameter disks as cathodes. The coin cell was assembled from a lithium foil with a thickness of 1.0 mm as the anode, and a Celgard 2400 separator between two electrodes. The electrolyte was  $1.0\ mol\ L^{-1} \quad lithium \quad bis(trifluoromethanesulfonyl) \quad imide \quad and$ 1.0 wt% lithium nitrate dissolved in 1,3-dioxolane and 1,2dimethoxyethane (v:v = 1:1). Approximately 20 and 45 µL of electrolyte was used in coin cells with the areal sulfur loadings of 1.1 and 2.6 mg cm<sup>-2</sup>, respectively. The electrodes were cut into  $3 \text{ cm} \times 5 \text{ cm}$  foils for pouch cell evaluation. All cells were assembled in a glove box protected by Ar atmosphere and tested in galvanostatic mode within a voltage window of 1.8-2.7 V using a LANHE multichannel battery test equipment. The specific capacity was calculated based on the mass of sulfur in the cathode. Electrochemical impedance spectroscopy (EIS) was performed on Solartron 1470E electrochemical workstation.

#### 2.4. Characterizations

The morphology of samples was characterized by a JEM 2010 (JEOL Ltd., Tokyo, Japan) transmission electron microscopy (TEM) operated at 120.0 kV and a JSM 7401F (JEOL Ltd.) scanning electron microscopy (SEM) operated at 3.0 kV. The samples after electrochemical cycling were dissembled in an Ar-protected glove box for further characterization. The pore-size distribution and Bru nauer–Emmett–Teller specific surface area of the samples were measured by  $N_2$  isothermal adsorption/desorption using Autosorb-IQ2-MP-C system. The pore size distribution and pore volume were calculated by quenched solid state density functional theory method using adsorption branch. The adhesion for electrodes with or without GNHs coating layer were tested by the lattice scraper with 3-mm and 1-mm interval between the blades. The contact-angle between cathode slurry and the current collector was tested with contact angle meter XG-CAM. Conductivity measurements were performed on disks using the KDY-1 four probe technique.

## 3. Results and discussion

### 3.1. Morphology of GNHs and Al/nanocarbon layer current collector

The GNHs are of a typical interconnected hybrid structure composed of graphene and CNTs [44]. Fig. 2a presented the TEM image of GNHs, in which both the structure of graphene sheets and CNTs can be observed and they are interconnected with each other. The GNH hybrid structures avoid the self-stacking of graphene and self-bundling of CNTs, respectively. Therefore, GNH materials are of self-dispersible property. The cross-linked structure of GNH materials can also bear mechanical compress and stretch, and maintain the structural stability. Moreover, the GNH units are interlinked through CNTs, which benefits the formation of 3D conductive networks.

The N<sub>2</sub> adsorption/desorption isotherm of GNHs is shown as Fig. 2b. The sharp increase at a low relative pressure ( $P/P_0$ ) region (below 0.05) and the hysteresis of  $P/P_0$  between 0.45 and 0.95 indicate the coexistence of micropores and mesopores in GNHs. GNHs possess a large mesopore volume of 1.46 cm<sup>3</sup> g<sup>-1</sup>. The pore size is mainly around 3–10 nm. The specific surface area of GNHs is calculated to be 1,188 m<sup>2</sup> g<sup>-1</sup>. Benefited from the hybrid structure and the highly porous structure, the GNH unit is highly conductive and with robust mechanical stability.

The fabrication of Al/nanocarbon layer current collector is compatible with the routine slurry coating process. Water, instead of organic solvents such as NMP, was applied as the solvent in favor of environmental benignity for the current slurry coating process. PVP, as a typical amphiphilic polymer, is applied as aqueous binder and disperser for GNH materials, and may especially benefit the performance of sulfur cathode by its polar affinity to polysulfide intermediates [45]. When coated onto the Al foil to form a cushion layer, the GNHs constituted a uniform porous interface (Fig. 2c). The thickness of the coating layer is  $4-5 \mu m$  (Fig. 2d), which can be facilely modulated by regulating the width of slit during coating process. The GNH units are interconnected with each other and tightly attached onto the Al foil surface to form an Al/nanocarbon layer current collector. The scalable fabrication of GNHs and the simple coating process can be easily scaled up for the bulk production of nanocarbon-coated Al foils as demonstrated in Fig. 2e.

## 3.2. Properties of Al/nanocarbon layer current collector

It is crucial to reduce the internal resistance in a battery system to achieve high energy efficiency, large power density, and high rate performance. This is also benefitted the cell with less ohmic heat generation, giving rise to safe battery with easy thermal management. Unlike the inter-particle conducting interfaces that have been extensively investigated, the interfaces between the active materials layer and Al foil are rarely concerned [46,47]. The introduction of super P carbon black [48,49] has been explored recently. Such an interface is very important with two major roles in both electron transfer and mechanical strength. With the introduction of a GNH coating layer in this contribution, both the electron transfer properties and affinity to the active materials can be therefore improved through the enhanced lateral electron transfer and increased contact area, respectively.

The influence of GNH coating layer on the interfacial electron transfer is revealed by direct measurement of electrical conductivity using the four-probe method (Fig. 3a). To exclude the impact of bulk Al as a metal conductor, insulating poly(ethylene) membrane was used to support the electrode materials with or without a GNH coating layer in between. The results turned out that the conductivity of electrode with a GNH coating layer reached around  $46 \text{ S m}^{-1}$ , which was about 2.7 times that without GNH coating layer ( $17 \text{ S m}^{-1}$ ). Obviously, the introduction of GNH layer enhances the conductivity of electrode materials, and is beneficial to reduce the overall resistance in a Li-S cell.

The surface affinity of Al/nanocarbon layer current collector to cathode slurry (NMP as solvent) was also altered by the GNH layer due to the introduction of carbonaceous layer and amphiphilic PVP agents. Fig. 3b illustrates the wetting properties of cathode slurry on Al foil current collectors with and without a GNH coating layer. The contact angle between the cathode slurry and Al/nanocarbon layer current collector is 41°, which is significantly smaller than that for cathode slurry on a pristine Al foil (85°). The reduced contact angle indicates an increased wetting capability on Al/nanocarbon layer current collectors, which favors the rapid coating process and renders the composite electrode with strong adhesion to underlayer current collector.

A scrape method was further applied on the electrodes to probe the difference in adhesion strength. Fig. 3c, d exhibits the optical photo of scraped electrode with or without a GNH coating layer, respectively. A lattice scraper with 3-mm interval between blades was employed. With electrode coating process, the cathode active materials layer attached firmly on the Al/nanocarbon layer current collectors (Fig. S1 online). Even after scraping and dust removal, the electrode with a GNH coating layer on Al foil stayed tightly attached (Fig. 3c). While for the electrode with a pristine Al foil. the electrode coating near the blades was almost broken apart and shed off from the Al foil (Fig. 3d). It was estimated that 30% of the Al foil area was exposed due to the detachment of electrode materials. The remaining electrode materials also became pulverized. In case of a lattice scraper with 1-mm interval, almost all electrode materials on the pristine Al foil were shed off, leaving a bare Al surface (Fig. S2 online). On the contrary, the electrode on an Al/nanocarbon layer current collector was attached on the current collector firmly. The GNH coating layer serves as an effective interlayer to bond Al foil and electrode together, and to avoid the cracking and shedding off of active materials. The robust mechanical stability can contribute to the long cyclic stability, especially in case of sulfur cathodes with large volume fluctuation nature.

#### 3.3. Electrochemical evaluation of Li-S cell applications

The electrochemical performance of both cathodes with Al/nanocarbon layer current collectors and pristine Al foil current collectors was evaluated. CNT/sulfur composite cathode materials were prepared with a sulfur content of 63% (on the basis of the weight of the whole electrode layer). The impact of GNH coating layer on improving the electric conductivity and reducing the polarization was consequently demonstrated.

Fig. 4a presents the long cyclic performance of cathodes at a current density of 0.5 C ( $1 \text{ C} = 1,675 \text{ mA g}^{-1}$  based on the mass of sulfur). The cathode with an Al/nanocarbon layer current collector exhibited an initial discharge capacity of 1,113 mAh g<sup>-1</sup>, corresponding to a sulfur utilization of 67%. The cathode without a GNH coating layer exhibited an initial discharge capacity of



**Fig. 2.** (Color online) Metal/nanocarbon layer current collectors. (a) TEM image of GNH materials; (b) N<sub>2</sub> isotherm, and corresponding pore size distribution (inset) of GNHs; (c) SEM images of Al/nanocarbon layer current collector (top view); (d) SEM cross-sectional view of Al/nanocarbon layer current collector; (e) picture of a roll of Al/nanocarbon layer current collector.



Fig. 3. (Color online) (a) Conductivities of sulfur cathodes with or without a GNH interfacial layer on the insulating substrate. (b) Contact angle for cathode slurry on Al foils with or without a GNH coating layer. Scape tests (blade interval 3 mm) of electrode with (c) a Al/nanocarbon layer current collector and (d) with a pristine Al foil.

844 mAh g<sup>-1</sup>. After 300 cycles, discharge capacities of 812 and 587 mAh g<sup>-1</sup> were preserved for cathodes with and without a GNH coating layer, corresponding to capacity retention of 73% and 69%, respectively.

The introduction of GNH coating layer in the Li-S cell also significantly reduced the polarization during the cycling. Fig. 4b presents the voltage profile of the 5th, 20th, and 40th cycle of Li-S cells with or without a GNH coating layer during cycling at 0.5 C. The middle



Fig. 4. (Color online) Long-cycle performance (a) and galvanostatic charge/discharge voltage profiles (b) of cells at 0.5 C. (c) Discharge MPV and energy efficiency of cells with or without a GNH coating layer.

point voltage (MPV, measured when the battery has discharged 50% of its total energy) difference (measured as the difference between charge and discharge voltages at MPV, as indicated in Fig. 4b) was chosen as a descriptor for the polarization. The MPV difference was reduced from 360 mV without GNH to 250 mV with GNH coating layers, and the corresponding MPV of the discharge curve was improved from 2.01 to 2.05 V (Fig. 4c).

Such an alleviated voltage hysteresis also contributes to improved energy efficiency, which is one long existing drawback for Li-S system. By taking voltage polarization into account, the energy efficiency is a more crucial indicator for large scale energy storage system ( $E = \int UIdt$ ). The energy efficiency was enhanced by ca. 85%–90% with an Al/nanocarbon layer current collector (Fig. 4c). The high energy efficiency originates from the high sulfur utilization with small polarization in a working cell.

With the enhanced electrode material/current collector interface, Li-S cells with an Al/nanocarbon layer current collector also presented remarkable rate capability. The Li-S cells were evaluated at different current densities from 0.05 to 2.0 C as shown in Fig. 5a. The discharge capacities were of 1,266, 959, 897, 826, 758, and 654 mAh g<sup>-1</sup> at 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 C, respectively, for the cell with an Al/nanocarbon layer current collector. At low testing current densities below 0.2 C, the Li-S cells with an Al/nanocarbon layer current collector exhibited increased capacity by 200– 300 mAh g<sup>-1</sup> compared to that with a pristine Al foil. At elevated current densities beyond 0.5 C, the cell with a pristine Al foil was not working. An extremely low capacity of 20 mAh g<sup>-1</sup> was observed at 2 C. The improved high rate performance is related to the enhanced electrical contact between current collectors and active materials through a very thin GNH coating layer.

The improved interface was also demonstrated by EIS (Fig. 5b). With an Al/nanocarbon layer current collector, the equivalent series resistance ( $R_e$ ) of the cell was reduced from 2.3 to 1.9  $\Omega$ . The semicircle in the Nyquist plots, corresponding to the charge transfer resistance ( $R_{ct}$ ) at interfaces, was remarkably reduced from 175

to 50  $\Omega$  through interfacing a GNH coating layer. Consequently, the charge transfer at interfaces in cell with an Al/nanocarbon layer current collector is much faster than in that with a pristine Al foil, indicating considerable enhancement in compatibility at high operation current densities.

# 3.4. Al/nanocarbon layer current collectors towards high-sulfurloading Li-S cells

Towards the improvement of sulfur loading amount to meet the demand of practical applications for an areal capacity of ca. 4 mAh g<sup>-1</sup> [50,51], achieving a mechanically stable interfaces between current collector and electrode materials becomes even more challenging [52–54]. The impact of GNH coating layer on the long-term stability was demonstrated in a cell with an areal sulfur loading of 2.6 mg cm<sup>-2</sup>. Fig. 6a displays the long-cycle curves of discharge capacity at a current density of 0.1 C. The cell with a GNH coating layer achieved an initial capacity of 918 mAh g<sup>-1</sup>, and maintained 64% of its initial capacity after 300 cycles. In contrast, a low initial capacity of 500 mAh g<sup>-1</sup> was obtained on a Li-S cell without a GNH coating layer. The capacity rapidly drops to below 300 mAh g<sup>-1</sup> after 30 cycles.

The postmortem examination of used cathodes was conducted (Fig. 6b). After 300-cycles test, the morphology of cathode with a GNH coating layer remained uniform and compact. The GNH coating layer possesses strong bonding simultaneously to Al foil and active materials, which prevents the mechanically failure during long term operation. On the contrary, the adhesion between Al foil and active materials was too weak to maintain a high loading amount of sulfur without a GNH coating layer, leading to the breaking apart and shedding off of electrode materials. A rapid performance fading within 30 cycles was therefore observed.

To demonstrate the performance of Al/nanocarbon layer current collector towards practical applications, pouch cell evaluations were conducted in 2 Ah pouch cells with an areal sulfur loading



Fig. 5. (Color online) (a) Discharge capacities at different current densities. (b) Nyquist plots of the EIS for cell with or without a GNH coating layer.



**Fig. 6.** (Color online) (a) Cyclic performance of cells at sulfur loading amount of 2.6 mg cm<sup>-2</sup>. (b) Postmortem examination of cells, showing the picture of cycled cathodes with and without GNH coating layer. (c) Voltage profile of 1st, 6th, and 12th cycle in 2 Ah pouch cell. (d) A photo of a pouch cell with an Al/nanocarbon layer current collector, lighting one LED.

amount of 7.2 mg cm<sup>-2</sup> in cathodes. Considering the areal loading of sulfur  $(7.2 \text{ mg cm}^{-2})$ , aluminum  $(4.2 \text{ mg cm}^{-2})$  in the cells, the GNH composite layer on Al foil introduces less than 1.5% extra weight. Fig. 6c presents the voltage profile of the 1st, 6th, and 12th cycle of 2 Ah pouch cells with pristine and Al/nanocarbon layer current collector. The GNH coating layer on Al foil contributes to enhanced initial specific discharge capacity in pouch cells from 691 to 787 mAh  $g^{-1}$  at 1st cycle. Meanwhile, the cell with GNH coating layer exhibited 771 mAh g<sup>-1</sup> at 12th cycle, namely 98% of the initial capacity. Notably, the major difference in specific capacity is induced by the low plateau capacities, which correspond to the liquid-to-solid conversion from Li<sub>2</sub>S<sub>4</sub> to Li<sub>2</sub>S<sub>2</sub>/Li<sub>2</sub>S in Li-S cells. The introduction of the metal/nanocarbon layer current collector remarkably facilitates conversion kinetics at a high areal sulfur loading condition. Moreover, the cell with pristine Al foil also suffer from rapid capacity fading to 611 and 536 mAh  $g^{-1}$  at 6th and 12th cycle, respectively. The pristine Al foil can hardly maintain the efficient electrical and mechanical contact between the current collector and active materials during electrochemical cycles, which led to the fast loss of active materials in the initial cycles. The 2 Ah pouch cell can light a red LED for a long time (Fig. 6d).

The carbon coated Al foil has been proposed for Li batteries and supercapacitors [46,47,55-58]. Herein, the application of Al/nanocarbon layer current collectors in Li-S batteries is investigated. The proposed Al/nanocarbon layer current collectors are of several merits. (1) The Al/nanocarbon layer current collector enhances the electric connections between active materials and the current collectors, lowering the interface resistance of electron transport. Therefore, the electrical conductivity of the cathodes can be enhanced from 17 to 46 S m<sup>-1</sup> with the introduction of GNH artificial interfaces. (2) The porous nanocarbon layer can host electrolytes and provide abundant lithium ions especially in operation conditions at high current densities. The specific capacity of the sulfur cathode is  $654 \text{ mA} \text{ hg}^{-1}$  with the Al/nanocarbon layer current collectors, which is over 30 times that of the cathode with pristine Al current collectors  $(20 \text{ mAh g}^{-1})$  at 2.0 C. (3) The nanocarbon artificial interfaces improved electron and ion transport behavior, leading to low interface resistance and rapid kinetics of electrochemical reactions, reduced overpotential (middle point voltage difference from 360 to 250 mV), and enhanced energy efficiency (ca. 85%-90%). (4) The Al/nanocarbon layer current collector also brings fast kinetics of conversion reactions mitigate the

dissolution of polysulfides into bulk electrolytes and hence suppress the shuttle of polysulfides. (5) The nanocarbon layer is tight attached to both Al foil and sulfur composites. Over 30% of the electrode will be removed by the scrape method, while no obvious peeling off of electrode can be observed with nanocarbon layer. (6) The stable structure of nanocarbon layer can cushion the repeated volume change of cathode and contribute to a longterm structural stability of the integrated cathode/current collectors. The aforementioned advantages of Al/nanocarbon layer current collectors lead to enhanced sulfur utilization with high energy efficiency and high cyclic stability in Li-S batteries.

With the nanocarbon coating layer with 3D hybrid structure of graphene and carbon nanotubes, their potential applications can be extended to other electrochemical battery systems that requires durable electrical and mechanical binding between electrode materials and current collectors. Moreover, the Al/nanocarbon layer current collectors can be facilely fabricated through a facile slurry coating process, which is highly compatible to current industrial manufacturing procedure of electrodes for rechargeable batteries.

## 4. Conclusions

We proposed a facile, scalable, and operable strategy to fabricate metal/nanocarbon layer current collectors to enhance the redox reaction in Li-S batteries. The highly conductive graphene/carbon nanotube hybrids were selected to attach onto Al foil to afford strong anchoring, interconnected electron pathways, and abundant electrolyte. Therefore, the GNH coating layer enhanced the interfacial behaviors and electrochemical performance for Li-S batteries. Li-S coin cells with a GNH coating layer exhibited an initial discharge capacity of 1,113 mAh  $g^{-1}$ , which was almost 300 mAh  $g^{-1}$  higher than those without GNHs layer (844 mAh  $g^{-1}$ ). The capacity retention was 73% for cells with a GNH coating layer after 300 cycles. A small MPV difference of 250 mV and a high energy efficiency of 90% were achieved as well, which outperformed routine cells (a MPV difference of 360 mV and an energy efficiency of ca. 85%). High rate capability and low charge transfer resistance were contributed from the GNH artificial interface. These results afford an emerging concept of enhancing electrochemical performance through industrially viable nanocarbonmodified current collectors for Li-S battery, which also holds a great promise for other electrochemical energy storage devices including supercapacitors, lithium-ion batteries, sodium-ion batteries, fuel cells, and flow batteries.

#### **Conflict of interest**

The authors declare that they have no conflict of interest.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.scib.2017.09.007.

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