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# Combination of Nitrogen-Doped Graphene with $MoS_2$ Nanoclusters for Improved Li-S Battery Cathode: Synthetic Effect between 2D Components

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ABSTRACT

Herein, a layer in layer nanocomposition of flower-shaped $MoS_2$ nanoclusters with nitrogen-doped reduced graphene oxide(N-RGO@$MoS_2$) has been successfully prepared by a facile hydrothermal method to build up 3D matrix for supporting sulfur. This approach will integrate the advantages and avoid the disadvantages of graphene and $MoS_2$ through synergetic effect to produce an outstanding Li-S battery cathode, such as high electronic conductivity of N-RGO to reach great rate performance; stronger interaction between $MoS_2$ and polysulfide to suppress the shuttle effect for an improved durability; the great compatibility between two 2D components avoids their self-aggregation to increase capacity through wrap around and adhesion effect with loaded sulfur. A series of samples with various content of $MoS_2$ are investigated to optimize the electrode performance. Finally, N-RGO@$MoS_2$-10/S delivers an optimal discharge capacity of 729.1 mAh $g^{-1}$ at 0.3C with the coulombic efficiency of 97.3% after 180 cycles.



## 1. Introduction

Lithium-ion batteries (LIBs) are one of the most important power sources in portable electronic devices and electric vehicles due to the high electromotive force, long cycling durability and high energy density [1–4]. Despite this, their wider application is restricted due to the limited energy density of available cathode materials in some special fields. New cathode materials need to be developed for meeting the request of higher energy density power source, among which sulfur is considered to be one of the most promising cathode for next-generation LIBs due to the high theoretical capacity (1672 mAh $g^{-1}$) [5], abundant reserves and nontoxic nature. However, the main drawbacks hindering Li-S battery practical application are followed: 1. poor conductivity of sulfur deteriorates batteries' rate performance; 2. volumetric change and polysulfide ($Li_2S_n$, 4< n <8) shuttling during cycling lead to the capacity degradation.

So far, a number of strategies have been tested to overcome the obstacles of sulfur cathode. One major improvement is made by employing conducting carbons to encapsulate sulfur to improve the conductivity of sulfur cathode and prevent the polysulfide shuttling simultaneously, such as porous carbon [6,7], graphene nanosheets [8–11], conducting polymers [12,13], hollow carbons [14,15] and carbon nanotubes [16,17]. Among these candidates, 2D graphene possesses outstanding performance due to high electrical conductivity and large surface area, which may help it to wrap around sulfur particles to build a conducting network resulting in larger capacity and better rate performance. Additionally, the volume change and polysulfide shuttling can be alleviated during cycling by the flexibility of conjugated graphene sheets, which leads to improved cycling performance. However, earlier study confirmed that these nonpolar carbon-based materials possess weak interaction with polar $Li_2S_n$ species, which can still lead to graduate capacity fading upon long-term cycle [18].

Recent studies have also given rising focus on metal oxides to bind polysulfide, such as $Al_2O_3$ [19], $SiO_2$ [20], $TiO_2$ [21] and $MnO_2$ [22], which typically contains strong polarized surface that composed by metal-oxygen bond to afford abundant polar active sites for absorption of polysulfide. The addition of oxide nanostructures as functional absorbents can effectively suppress the shuttle effect of Li-S batteries. Compared to nonconductive metal oxide, some metal sulfides have better conductivity attributed to

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the denser electron atmosphere and unique band structures. Additionally, metal-sulfur bonds can better bind polysulfide through stronger S···S interaction and dipolar interaction of metal-sulfur bonds on polarized surface.

2D layered metal sulfides with analogous structures to graphite, such as $MoS_2$ [23], $WS_2$ [24] and $SnS_2$ [25] have been proved an outstanding performance as LIBs electrode. As candidate materials of Li-S cathode, the open framework of these types of materials offers large surface area and allows a better connection with sulfur particles through wrap around and adhesion effect. Especially, $MoS_2$ have been proven to be highly efficient in depressing polysulfides shuttle to a longer cycle stability. Cui et al. [26,27] confirms that there are strong binding energies between $Li_2S$ and the edge sites of $MoS_2$. Xing et al. [28] synthesizes hierarchical $MoS_2/SnO_2$ nanocomposites and confirms that $MoS_2$ can increase the conductance of the composites.

Therefore, the low cost, readily available 2D metal sulfide-$MoS_2$ has been combined with reduced graphene oxide (RGO) by a facile hydrothermal method to build up conductive matrix for Li-S battery in here. This approach would integrate the advantages and avoid the disadvantages of graphene and $MoS_2$ through synergetic effect to produce an outstanding Li-S battery, such as high electronic conductivity of RGO to reach great rate performance; $MoS_2$ as functional absorbents to suppress the shuttle effect of polysulfide to improve battery's durability; the layer in layer structure of two 2D components avoids their self-aggregation to increase capacity of cathode through enlarged surface area for sulfur loading.

## 2. Experimental

### 2.1. Preparation of N-RGO/S

Graphite oxide was first prepared from graphite powder via a modified Hummers' method [29] reported elsewhere. Afterwards, graphite oxide was exfoliated in water with ultrasonic treatment for 4 h to form a colloidal suspension (100 mL, 2 mg $mL^{-1}$). Then, sulfourea was dissolved into the suspension and then transferred and sealed into Teflon-lined stainless steel autoclave, which was heated at 200 °C for 20 h in a constant temperature oven. After cooling down to ambient temperature naturally, the samples were finally dried in the freeze dryer.

The N-RGO/S composites were prepared through a melt-diffusion technique. Typically, the sublimed sulfur and N-RGO at mass ratio of 65:35 were added to the $CS_2$ to form a uniform dispersion solution, then dried under magnetic stirring at 45 °C. Afterwards, the dried sample put into a sealed vacuum glass tube, then the glass tube put into quartz tube furnace in $N_2$ atmosphere and kept the temperature at 155 °C for 12 h. The final N-RGO/S was obtained by further treatment at 200 °C for 2 h under $N_2$ condition to remove redundant sulfur from the surface of the composites.

### 2.2. Preparation of N-RGO@$MoS_2$-n/S

200 mg graphite oxide was exfoliated in a mixture of 50 mL deionized (DI) water and 50 mL ethylene glycol with ultrasonic treatment for 4 h to form a colloidal suspension. 33.6 mg $Na_2MoO_4{\cdot}2H_2O$, 80 mg $(NH_2)_2CS$, and 15 mg polyethylene glycol (PEG-20000) were successively dissolved into another 30 mL DI water and then stirred for 0.5 h. Afterwards, the two solutions were mixed together under vigorous stirring. Subsequently, this mixed solution was transferred and sealed into Teflon-lined stainless steel autoclave, which was heated at 200 °C for 20 h in a constant temperature oven and then cooled down to ambient temperature naturally. Finally, the precipitate powder was centrifuged and washed several times with ethanol and DI water, and dried in the freeze dryer.

By adjusting amount of $Na_2Mo_2O_4{\cdot}2H_2O$, we synthesized N-RGO@$MoS_2$ composites as controling samples with various $MoS_2$ mass contents of 25%, 10% and 5%, which were labelled as N-RGO@$MoS_2$-25, N-RGO@$MoS_2$-10, N-RGO@$MoS_2$-5, respectively.

The N-RGO@$MoS_2$/S composites were prepared through a melt-diffusion technique as mentioned above. The sulfur filled composites with different $MoS_2$ contents were labelled as N-RGO@$MoS_2$-25/S, N-RGO@$MoS_2$-10/S, N-RGO@$MoS_2$-5/S, respectively.

### 2.3. Adsorption capability

0.05 M polysulfide solution was prepared with mixing $Li_2S_6$ and DME/DOL. The samples were dried for 12 h under vacuum; 25 mg sample was placed into 5 mL of the lithium polysulfide solution in an argon-filled glove box for 24 h to adsorption equilibration.

### 2.4. Samples characterization

The structures and morphologies of obtained composites were characterized with X-ray diffraction (XRD, X'Pert PRO MPD, Holland), field emission scanning electron microscopy (FE-SEM) (Hitachi S-4800, Japan), and transmission electron microscopy (TEM, JEM-2100UHR, Japan). Nitrogen sorption isotherms were measured at 77 K with an ASAP 2020 analyzer (Micromeritics, US). The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption data. The pore size distribution was calculated by the density functional theory (DFT) method from the adsorption branches of the isotherms. The functional groups in the samples were studied by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALab250Xi). The weight ratio of sulfur in the composite was determined by thermogravimetric analysis (TGA, STA 409 PC Luxx, Germany).

### 2.5. Electrochemical measurements

The electrochemical measurements were conducted using CR2032 coin cells with pure Li foil as the counter and reference electrode at room temperature. Working electrodes consist of obtained samples, carbon black and polyvinylidene difluoride in a weight ratio of 7:2:1 in N-methyl-2-pyrrolidinone. The slurry was coated onto a current collector made from aluminium foil and then was dried under vacuum at 60 °C for 12 h. The electrodes were cut to disks typically with a diameter of 12 mm, and the average mass of the sulfur loading within the coin cells is around 1.5-2.0 mg $cm^{-2}$. The cells assembly were carried out in an Ar-filled glovebox with the concentration of moisture and oxygen below 0.1 ppm. The separator was microporous polypropylene and the organic electrolyte was composed of 1.0 M LiTFSI in 1,2-dimethoxyethane and 1,3-dioxolane (DME/DOL, 1:1 vol) with 1.0% $LiNO_3$ (analytical grade). The galvanostatic discharge-charge cycle tests and rate tests were carried out on a Land Battery Measurement System (Land CT2001A, China) at various current densities of 0.3-4C (1C = 1672 mA $g^{-1}$) with a cutoff voltage of 1.5-3.0 V vs. $Li/Li^+$ at room temperature. The specific capacity was calculated based on the mass of sulfur. Cyclic voltammetry (CV) curves were conducted using an Ametek PARSTAT4000 electrochemistry workstation between 1.5 and 3.0 V at a scan rate of 0.1 mV $s^{-1}$. Electrochemical impedance spectroscopy (EIS) tests were also performed using Ametek PARSTAT4000 electrochemistry workstation in the frequency range of 100 kHz to 10 mHz with AC voltage amplitude of 10 mV.