

Highly dispersed sulfur in multi-walled carbon nanotubes for lithium/sulfur battery

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Abstract A facile method is developed for homogeneous dispersion of sulfur (S) nanoparticles in multi-walled carbon nanotubes (MWCNTs). The process involves the modification of MWCNTs via oxidation catalyzed by acid and the introduction of sulfur nanoparticles into the MWCNTs through direct precipitation. The resulting sample (precipitated S/MWCNTs) is characterized with scanning electron microscopy and thermogravimetric analysis, and its performance as cathode of lithium/sulfur battery is investigated with a comparison of the sample prepared by ball-milling (ball-milling S/MWCNTs). It is found that the precipitated S/MWCNTs exhibit better battery performance than the ball-milling S/MWCNTs. The initial discharge capacity is 1,299 mAhg⁻¹ for the precipitated S/MWCNTs but only 839 mAhg⁻¹ for ball-milling S/MWCNTs at 0.02 C. The capacity remains 800 mAhg⁻¹ for the precipitated S/MWCNTs but only 620 mAhg⁻¹ for ball-milling S/MWCNTs at 0.05 C after 50 cycles. The better performance of the precipitated S/MWCNTs results from the improved uniformity of S dispersed in MWCNTs through precipitation.

Keywords Multi-walled carbon nanotubes · Sulfur · Precipitation · Cathode · Lithium/sulfur battery

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Introduction

The development of lithium-ion batteries (LIBs) with high energy, high power density, and high safety is in great demand for extending their applications from powering electric vehicles to storing electricity from renewable energy [1]. A storage system based on lithium/sulfur (Li/S) battery might be the most promising candidate for the next generation LIBs. Li/S battery has a theoretical capacity of 1,672 mAhg⁻¹ and a theoretical energy density of 2,600 Whkg⁻¹, which is about five times higher than that of the LiCoO₂/graphite and LiFePO₄/C systems [2–4]. Moreover, sulfur is abundant in various minerals, cheap, and environmental friendly.

However, Li/S battery still has not been commercialized yet, despite its excellent properties. Its poor cycle life is the main hindrance toward its commercialization, which results from the low electronic and ionic conductivity of sulfur (S) and the easy dissolution of the reaction intermediates, polysulfides, generated during charging and discharging. The element sulfur has a low conductivity, $5 \times 10^{-30} \text{ Scm}^{-1}$ and thus is almost electrically and ionically insulated, leading to poor electrochemical accessibility and a low utilization of sulfur in the electrode. The shuttle mechanism lowers the efficiency of Li/S battery by dissolution, migration, and parasitic reactions of polysulfides [5–7].

Much effort has been made to solve these problems, and many methods have been proposed, including optimizing electrolytes [8–11] and designing cathode materials such as sulfur/polymer composites [12–16] and sulfur/carbon composites [17–22]. New electrolytes are helpful to reduce the dissolution of polysulfides but cannot improve the conductivity of sulfur. Differently, the application of sulfur composites, especially sulfur/carbon composites, is found to be effective for reducing the polysulfide dissolution and improving the sulfur conductivity, because carbon materials provide sulfur with conductive network [23–31].

Multi-walled carbon nanotubes (MWCNTs), due to their large chemically active surface and exciting electronic and mechanical properties, have been used as support materials to prepare sulfur/carbon composites. It has been known that the MWCNTs are useful carbon materials for the dispersion and stabilization of sulfur nanoparticles. In the previous researches, S/MWCNT composites were synthesized via ball-milling [5, 32], heat treatment [21, 23], and solvent-exchange methods [22, 27, 33]. The methods for the preparation of these composites are complicated, though the composites exhibit good performance.

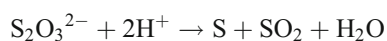
In this work, we developed a facile method for the preparation of S/MWCNT composite. In this method, highly dispersed sulfur nanoparticles were embedded in MWCNTs, denoted as precipitated S/MWCNTs, through a simple chemical reaction–deposition strategy. A conventional S/MWCNT composite was also prepared by ball-milling, denoted as ball-milling S/MWCNTs for comparison.

Experimental

Preparation of S/MWCNTs

The raw MWCNTs (purchased from Chengdu Institute of Organic Chemistry of CAS) were initially dispersed in concentrated hydrochloric acid for 24 h at room temperature. Then, the pretreated MWCNTs were refluxed in the mixture of concentrated nitric acid and sulfuric acid (1:3 by vol.) at 80 °C for 6 h and washed by distilled water until the pH value reached 7.0. After filtration, the modified MWCNTs were dried at 80 °C for 24 h in a vacuum oven.

The precipitated S/MWCNTs were prepared through the direct precipitation method. Specially, 0.5 g of MWCNTs was first dispersed in 150 ml distilled water under sonication at 50 °C for 8 h to obtain a homogeneous suspension. Then, a solution containing 16 g sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, Tianjin Damao Chemical Reagent Factory) and 5 wt% surfactant hexadecyltrimethylammonium bromide (99 %, Aladdin) was added into the suspension under magnetic stirring. The mixed solution was sonicated for 2 h; 100 ml of 2 mol/l formic acid (HCOOH , 88 %) solution was added dropwise under stirring. Finally, the precipitate was filtrated, washed with acetone and distilled water several times, and dried at 50 °C in a drying oven for 72 h. The reaction process for the sulfur preparation is as follows [29]:



The ball-milling S/MWCNTs were fabricated via mechanical ball-milling process. The weight ratio of sulfur (99.95 %, Aladdin) to MWCNTs is 2:1 and the mixture was then ground with *N*-methylpyrrolidone (NMP) as

dispersant for 5 h. All the as-synthesized S/MWCNT samples were heat-treated in tube furnace at 155 °C for 12 h with a heating rate of 5 °Cmin⁻¹ under flow argon atmosphere, which favors the diffusion of sulfur into the MWCNTs.

Preparation of the sulfur cathodes

The sulfur cathodes were prepared as follows. Active materials (the precipitated and ball-milling S/MWCNTs), acetylene black, and polyvinylidene difluoride with a weight ratio of 80:10:10 were mixed in NMP. The slurry was coated on an aluminum current collector. Then, the coated electrodes were dried in a vacuum oven at 60 °C for 48 h until the solvent was completely evaporated. The electrode was subsequently pressed with a twin roller and the final thickness of the coated composite cathode was approximately 50 μm. The electrodes were cut into a 1 × 1-cm size.

Physical measurements

The morphology of materials was observed using scanning electron microscopy (SEM, Zeiss Ultra 55). The content of the sulfur in the prepared S/MWCNT composites was determined by thermogravimetric analysis (PerkinElmer TGA 7) under N₂ atmosphere from room temperature to 500 °C at a heating rate of 5 °Cmin⁻¹.

Electrochemical measurements

To evaluate the electrochemical properties of the prepared S/MWCNT composites, CR2025-type coin cells were assembled in an argon-filled glove box with H₂O and O₂ content lower than 1 ppm, using lithium foils as the counter electrodes, microporous polypropylene membrane (Cellgard 2300) as separator, and 1.0 M LiN(CF₃SO₂)₂ (LiTFSI, 99.95 %, Aladdin) dissolved in dimethoxyethane (99.95 %, Aladdin) and dioxolane (99.95 %, Aladdin) (1:1, v/v) as the electrolyte. Cyclic voltammetric measurements were performed on Solartron-1480 (England) between 1.5 and 3 V (vs. Li/Li⁺) at a scanning rate of 0.1 mVs⁻¹. The coin cells were charged and discharged using a LAND cell test system (Land CT 2001A, China) between 1.5 and 3 V (vs. Li/Li⁺) at room temperature.

Results and discussion

The structure characterization

Figure 1 shows the SEM images of treated MWCNTs, precipitated S/MWCNTs, and ball-milling S/MWCNTs. Compared with the treated MWCNTs (Fig. 1a), it can be

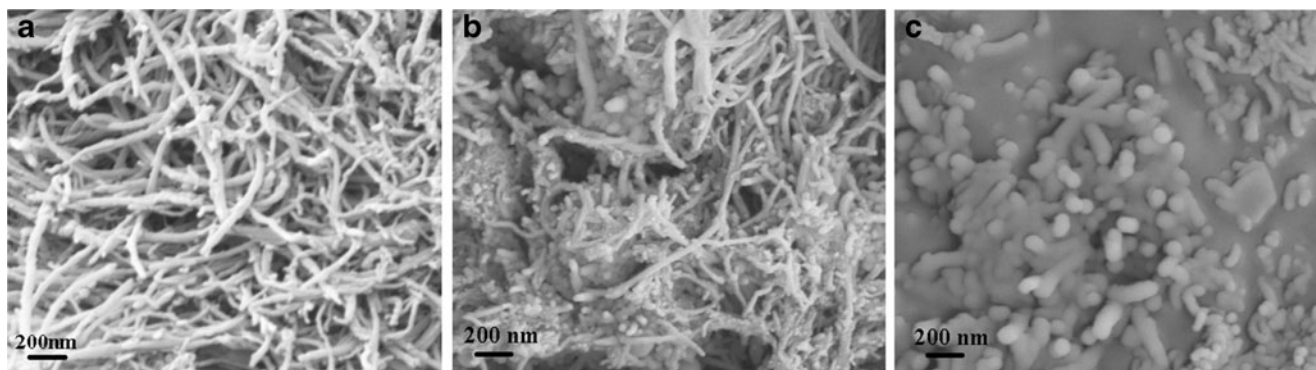


Fig. 1 SEM images of treated MWCNTs (a), precipitated S/MWCNTs composite (b), and ball-milling S/MWCNTs composite (c)

known that S and MWCNTs have been combined together (Fig. 1b, c). As can be seen from Fig. 1, the sulfur in precipitated S/MWCNTs was highly dispersed in multi-walled carbon nanotubes (Fig. 1b), while the sulfur in ball-milling S/MWCNTs was agglomerated (Fig. 1c). The treated MWCNTs with many functional groups, such as hydroxyl, carboxyl, and carbonyl [34], provide sulfur with growth points when the sulfur precipitated through the chemical reaction–deposition strategy and a subsequent low-temperature thermal treatment process. The functional groups on MWCNTs also provide an intimate contact between sulfur and MWCNTs. There is an interaction between sulfur and oxygen-containing groups such that the functional groups can anchor sulfur atom, which has been confirmed by theoretical calculation in the previous report [24]. However, ball-milling is a physical process, in which the functional groups on MWCNTs make no sense for the sulfur dispersion. Therefore, the modified MWCNTs are introduced as sulfur-fixed matrix and conducting materials and the highly dispersed sulfur can be expected to exhibit good performance as cathode of lithium/sulfur battery.

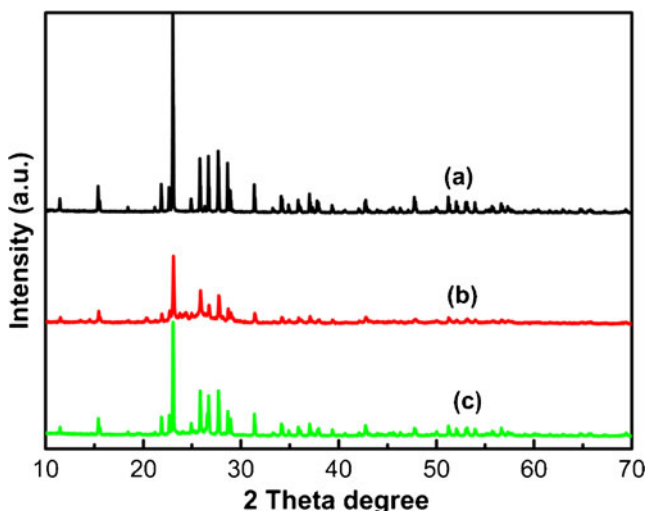


Fig. 2 X-ray diffraction patterns of pure sulfur (a), precipitated S/MWCNTs (b), and ball-milling S/MWCNTs (c)

Figure 2 presents the X-ray diffraction (XRD) patterns of the precipitated and the ball-milling S/MWCNTs compared with pure sulfur. Pure sulfur exhibits several sharp peaks from 10° to 60°, indicating that it has good crystallinity. Both precipitated and ball-milling S/MWCNTs have similar XRD patterns to the sublimed sulfur except for the appearance of the slight and broad MWCNT peaks centered at $2\theta = 26^\circ$, confirming that the sulfur has been successfully combined into the MWCNTs. Among the three samples, the precipitated S/MWCNTs have the weakest diffraction peaks, suggesting that sulfur in the precipitated S/MWCNTs is dispersed in MWCNTs more uniformly than the sulfur in the ball-milling S/MWCNTs.

Sulfur content in S/MWCNTs

Figure 3 shows the thermogravimetric analysis (TGA) curves of the pure sulfur and S/MWCNT composites under N₂ atmosphere, from room temperature to 500 °C at a heating rate of 5 °Cmin⁻¹. The sulfur evaporation takes place at 150 °C and the evaporation is completed at 280 °C, as shown by the TGA

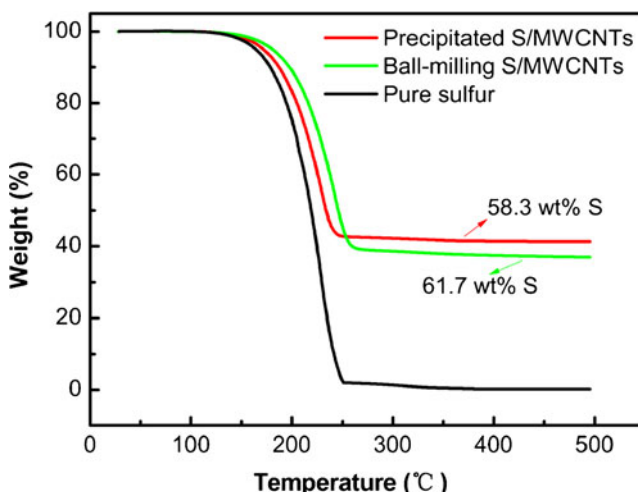


Fig. 3 TGA curves of the precipitated S/MWCNT and the ball-milling S/MWCNT composite

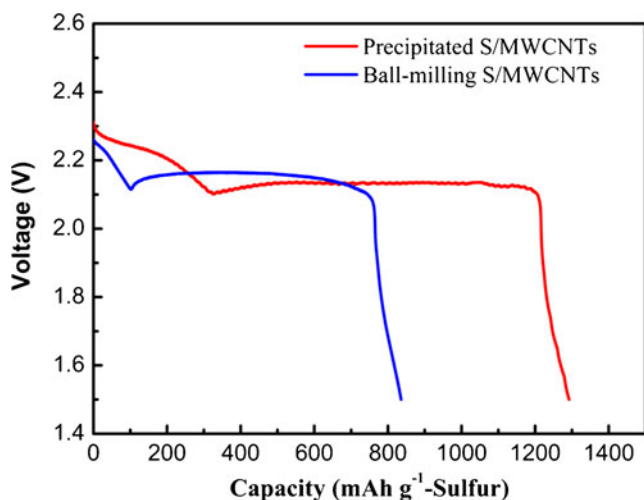


Fig. 4 Galvanostatic initial discharge profiles at 0.02 C of the precipitated S/MWCNT and ball-milling S/MWCNT composite electrodes

curve of the pure sulfur. The sulfur loss can be observed by comparing the TGA curves of the composites with that of the pure sulfur, and the sulfur contents in the composites can be determined by the weight loss. The sulfur content in both composite is equivalent, 58.3 wt% for the precipitated S/MWCNTs and 61.7 wt% for the ball-milling S/MWCNTs. In the preparation of the precipitated S/MWCNTs, the weight ratio S to MWCNTs is 4:1, which is larger than that in the product. The lower content of sulfur in the resulting composite (58.3 wt%) can be ascribed to the inevitable loss of S during preparation.

Electrochemical performance of S/MWCNT composites

The initial discharge–charge curves of the sulfur cathodes with the precipitated S/MWCNTs and ball-milling S/MWCNTs at 0.02 C are shown in Fig. 4. As can be seen from

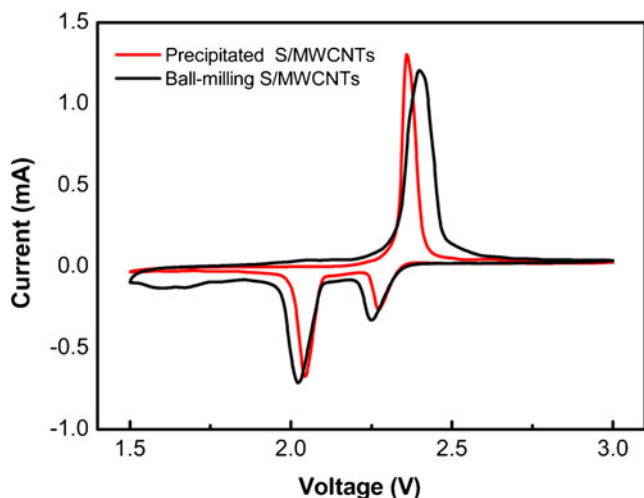


Fig. 5 Cyclic voltammograms of the precipitated S/MWCNT composite and ball-milling composite electrodes at a scanning rate of 0.1 mV s^{-1}

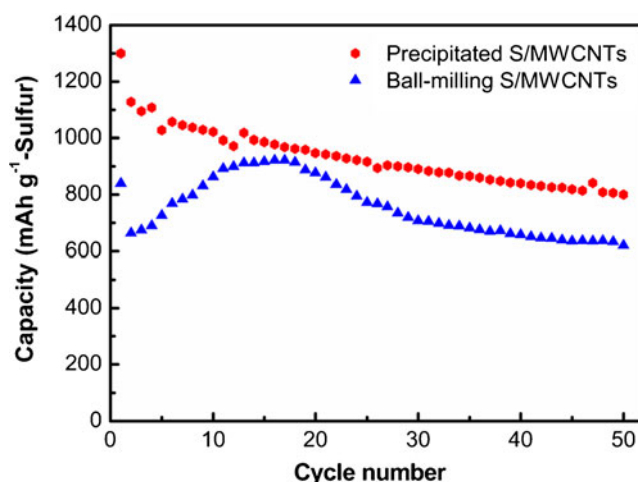


Fig. 6 Cycling performance of the precipitated S/MWCNT and ball-milling S/MWCNT electrodes at 0.05 C

Fig. 4, there two discharge steps that can be observed for both sulfur cathodes. One is at about 2.25 V and the other is at about 2.05 V. The former is attributed to the reduction of S_8 to the high-order lithium polysulfides (Li_2S_n , $n \geq 4$) and the latter to the reduction of high-order lithium polysulfides to low-order lithium polysulfides (Li_2S_2 , Li_2S) [20, 29, 35]. The initial discharge specific capacity of the precipitated S/MWCNTs electrode is about $1,292 \text{ mAh g}^{-1}$ at 0.02 C, which means that the utilization of electrochemically active sulfur is about 77%. However, the ball-milling composite shows only about 830 mAh g^{-1} in its first discharge profile. Therefore, the cathode with precipitated S/MWCNTs shows a better utilization of sulfur than the cathode with ball-milling S/MWCNTs.

It can be noted from Fig. 4 that there is less polarization of milled composite than that of the precipitated composite during the second discharge step. This phenomenon can be ascribed to the accumulated reaction products after the first discharge step, which might increase the electrode resistance. The milled composite shows far larger polarization than the

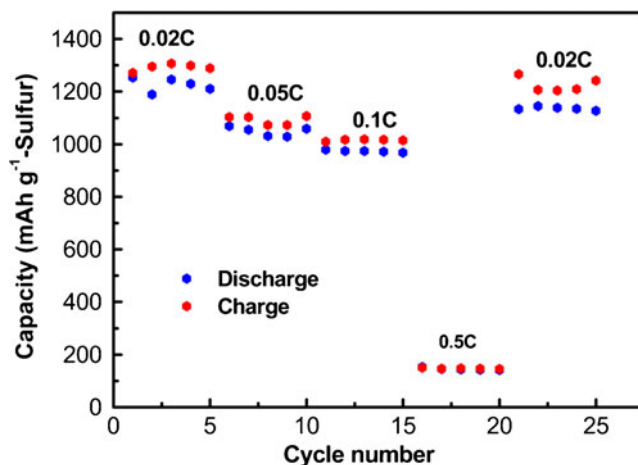


Fig. 7 Rate performance of the precipitated S/MWCNT cathode

precipitated sulfur and delivers less than half of the capacity of the precipitated composite after the first discharge step, resulting in less accumulated reaction products and smaller electrode resistance in the milling composite.

Figure 5 presents the cyclic voltammograms of the Li/S batteries with two S/MWCNT composite electrodes at a scan rate of 0.1 mVs^{-1} . From Fig. 5, we can see two cathodic peaks, which are corresponding to the formation of long-chain polysulfides (Li_2S_n , $8 \geq n \geq 4$) at 2.25 V and short-chain Li_2S_2 , even Li_2S at 2.05 V, as demonstrated in the galvanostatic measurements (Fig. 4). Two expected oxidation peaks overlap to form one large peak at about 2.4 V [20, 24, 25, 35, 36]. The potential difference between the peak couple of the precipitated S/MWCNTs is smaller than that of ball-milling S/MWCNTs, indicating that the electrochemical polarization of the ball-milling S/MWCNTs is stronger than that of the precipitated S/MWCNTs.

Figure 6 presents the cycle performances of the Li/S batteries with the precipitated S/MWCNT and ball-milling S/MWCNT composites as cathodes. The initial discharge capacity of the two samples was about 1,299 and 839 mAhg^{-1} at 0.02 C. The subsequent cycles were performed at 0.05 C. The precipitated S/MWCNT composite displays a discharge capacity of $1,128 \text{ mAhg}^{-1}$ at 0.05 C, which remains 800 mAhg^{-1} after 50 cycles. Differently, the ball-milling S/MWCNT cathode displays a discharge capacity of 663 mAhg^{-1} at 0.05 C. The reversible capacity of the ball-milling S/MWCNT cathode shows a gradual increase before the first 15 cycles. This phenomenon can be attributed to the improved electronic conductive MWCNTs covered with the insulating sulfur when sulfur changes from a solid state to the dissolved polysulfide state due to the redox reaction of the surface sulfur-contacting electrolyte [5]. After 50 cycles, the capacity of the ball-milling S/MWCNT cathode remains 620 mAhg^{-1} . The precipitated S/MWCNT composite delivers larger capacity than the ball-milling S/MWCNT composite during cycling. It is obvious that the better performance of the precipitated S/MWCNT composite results from the highly dispersion of sulfur formed through direct precipitation.

The rate capability of the precipitated S/MWCNT composite is demonstrated in Fig. 7. The composite delivers a reversible capacity of $1,210 \text{ mAhg}^{-1}$ at a low rate of 0.02 C after 5 cycles. The reversible capacity remains 140 mAhg^{-1} at 0.5 C after 20 cycles of various rates and resumes to $1,145 \text{ mAhg}^{-1}$ at 0.02 C. This result suggests that the precipitated S/MWCNT electrode has a high interface kinetic activity and favorable electrode stability against volume expansion.

Conclusions

A facile method for the preparation of S/MWCNT composite was proposed in this paper. Sulfur can be well dispersed

on MWCNTs via direct precipitation route. As-prepared S/MWCNT composite shows better electrochemical performance: delivers a discharge capacity as high as $1,299 \text{ mAhg}^{-1}$ at 0.02 C and exhibits good cyclic stability and rate performance.

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