

Sulfur–amine chemistry-based synthesis of multi-walled carbon nanotube–sulfur composites for high performance Li–S batteries†

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We report a sulfur–amine chemistry-based method to prepare multi-walled carbon nanotube–sulfur (MWNT–S) composites in a highly efficient and quantitative manner. The resulting MWNT–S composites exhibit excellent cycling stability at up to 400 cycles, with high sulfur loading. Developing this method also increases the number of research routes that could be pursued with respect to Li–S batteries.

The lithium–sulfur (Li–S) battery is one of the most promising rechargeable battery systems for large-scale energy storage applications that require high energy density, because of their high theoretical specific capacity of 1672 mA h g^{−1} and the low cost and natural abundance of sulfur.^{1–3} Various carbon–sulfur (C–S) composites have been prepared as the active cathode material to address the outstanding challenges of Li–S battery technology, such as the electrical insulating nature of sulfur and the polysulfide shuttle mechanism. Conducting carbon materials with high porosity and/or a large specific surface area, such as active carbon,^{2,4} graphene⁵ and carbon nanotubes,^{6–9} have been widely explored for Li–S applications.

Most of the C–S composites used in Li–S batteries are prepared *via* mechanical pre-mixing and thermal treatment methods.^{7,9} This is straightforward to scale up, but the mechanical pre-mixing and thermal annealing steps are highly energy- and time-consuming, and sulfur vapor is corrosive and environmentally unfriendly under high temperatures.³ Furthermore, it is difficult to control the homogeneity of sulfur coverage on the carbon matrix in the pre-mixing and heating process.

Recently, solution deposition methods have emerged for the preparation of sulfur materials in the Li–S battery. For example,

chemical processes involving the decomposition of polysulfide or thiosulfate^{10,11} and physical processes involving precipitation of sulfur from CS₂ solutions in poor solvents have been developed.¹² Solution-based methods have advantages with respect to sulfur morphology control, but issues such as the preparation of sulfur precursors, post-reaction processing, and quantitative loading of sulfur need to be improved.

Here, we report a sulfur–amine chemistry-based method to prepare MWNT–S composites as cathode materials for Li–S batteries. Sulfur–amine complexes have been previously used as sulfur sources for the preparation of metal sulfide nanocrystals.¹³ We find that these complexes can be used to deposit sulfur on MWNTs in a quantitative manner, without complicated pre- and post-treatments. The resulting MWNT–S composite shows a uniform coating of sulfur on the MWNT matrix, leading to high capacity and long cycle stability for Li–S batteries. Compared to thermal treatment and solution deposition methods previously reported, this method is low energy consumption, time-saving, low cost and easy to scale-up.

As illustrated in Fig. 1, elemental sulfur firstly reacts with ethylenediamine (EDA) to form a S–EDA complex precursor solution (Fig. S1, ESI†). The precursor solution is then slowly added to a MWNT dispersion in diluted hydrochloric acid. The S–EDA precursor decomposes in the diluted hydrochloric acid and octatomic S₈ molecules are recovered. The freshly-recovered sulfur molecules deposit on the surface of the MWNT, forming the MWNT–S composite with a core–shell structure. These MWNT–S composites can be

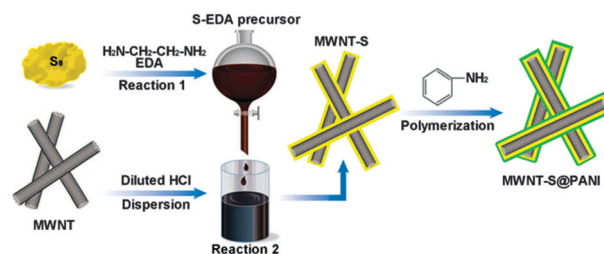


Fig. 1 Schematic diagram for the preparation of MWNT–S and MWNT–S@PANI composites *via* the sulfur–amine chemistry-based method.

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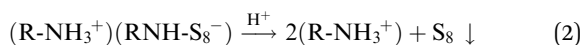
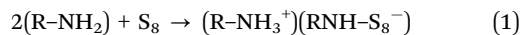
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further coated with polyaniline (PANI) *via in situ* polymerization to form MWNT-S@PANI composites.

Sulfur-amine chemistry was first investigated in the 1960s to understand why the solubility of sulfur in amine solvents was much higher than predicted by either empirical or theoretical considerations.¹⁴ It was revealed that in amine solutions sulfur mainly exists as polysulfide ions and sulfur radical ions, instead of octatomic molecules.^{15,16} As shown in eqn (1), direct nucleophilic attack of nitrogen opens the octatomic ring of S₈ and forms open chain alkylammonium polysulfides.^{16,17}



Spectroscopic analysis of the S-EDA solution in our experiments agrees with the reaction mechanism. The ultraviolet-visible (UV-vis) absorption spectrum of the S-EDA precursor is shown in Fig. 2a. The peaks at 616, 400 and 316 nm indicate the presence of sulfur radical ions ($-\text{S-S}_x-\text{S}^\bullet$) and polysulfides.^{14,18} Raman spectra in Fig. 2b show new peaks at 536, 440 and 397 cm⁻¹ after the dissolution of sulfur in EDA, which are also attributed to polysulfide ions and radical ions.^{15,19}

Octatomic sulfur can be quantitatively recovered from sulfur-amine solutions upon addition to diluted hydrochloric acid (Reaction 2).¹⁴ Raman spectra in Fig. 2b show that all peaks corresponding to polysulfide ions and radical ions completely disappear when S-EDA is mixed with acid, while three new peaks at 474, 221 and 153 cm⁻¹ corresponding to octatomic S₈ molecules appear.^{15,20}

We took advantage of Reactions 1 and 2 to disperse S on the MWNT matrix for Li-S battery applications. Since the sulfur can be fully recovered from the S-EDA precursor, the amount of sulfur load in the conducting matrix can be controlled quantitatively. As shown in Fig. 2c, for MWNT-S composites with MWNT to nominal sulfur ratios of 1:2, 1:3, 1:4 and 1:5 (w/w), the actual sulfur loads measured by thermogravimetry (TG) are 64.5%, 72.8%, 77.8% and 81.2%, respectively. Fig. 2d shows that the actual sulfur load is

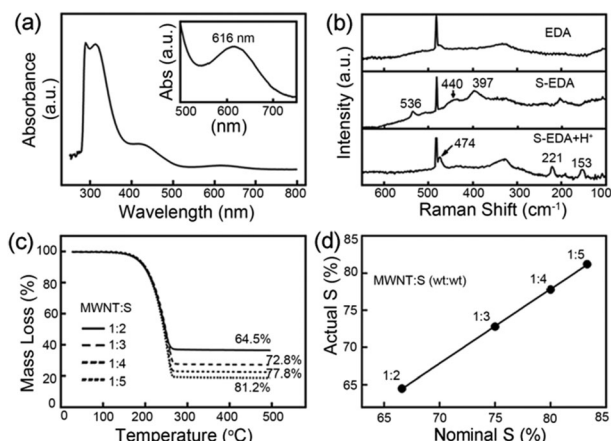


Fig. 2 (a) UV-vis spectrum of the S-EDA precursor; (b) Raman spectra of EDA, the S-EDA precursor and the S-EDA precursor mixed with diluted hydrochloric acid; (c) thermogravimetry (TG) analysis of MWNT-S composites prepared with different MWNT to sulfur ratios; (d) linear correlation between nominal sulfur and actual sulfur content in MWNT-S composites.

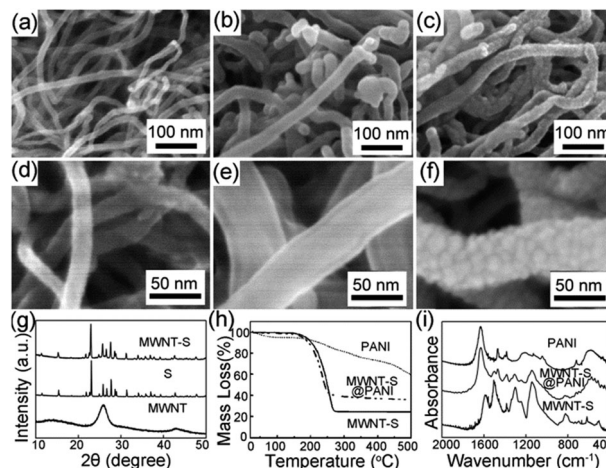


Fig. 3 Scanning electron micrographs of (a and d) the MWNT, (b and e) the MWNT-S composite, and (c and f) the MWNT-S@PANI composite. To avoid charging during SEM imaging, MWNT-S and MWNT-S@PANI samples were decorated with 6 nm Au by sputtering. (g) XRD patterns of the MWNT, S and the MWNT-S. (h) TG analyses and (i) Fourier transform infrared (FTIR) spectra of PANI, and the MWNT-S and MWNT-S@PANI composites.

linearly correlated to the nominal sulfur load with a slope of 1.00. The small loss of sulfur of around 2.2% may be attributed to the generation of H₂S or thioamide and/or transfer loss in the overall process.¹⁴

Morphological and spectral characterizations reveal that the MWNT-S composite has a homogeneous core-shell structure with a thin sulfur shell. Fig. 3a-f show the scanning electron microscopy (SEM) images of the MWNT, the MWNT-S and the MWNT-S@PANI. MWNT-S and MWNT-S@PANI composites were prepared with a nominal S:MWNT ratio of 4:1 (these composites were also used for electrochemical analysis in later sections). Considering the sputtered Au layer on the MWNT-S and MWNT-S@PANI composites for SEM, the sulfur layer on the MWNT is about 6–8 nm in thickness (also see Fig. S4, ESI†). After coating the MWNT-S composite with a PANI layer, the diameter became a little thicker, and the surface became rougher, with hemispheric particles protruding from the surface (Fig. 3c and f).²¹ Fig. 3g shows that the sulfur in the MWNT-S composite exhibits the same XRD pattern as pure elemental S, indicating that the sulfur loading process onto the MWNT does not induce any changes in crystal structure. TG analysis, as presented in Fig. 3h, shows that the sulfur content in the MWNT-S and MWNT-S@PANI composites is 77.8% and 65%, respectively. Fig. 3i shows FTIR spectra of pure PANI, and the MWNT-S and MWNT-S@PANI composites. The new peaks of the MWNT-S@PANI composite compared to the MWNT-S are similar to pure PANI, which also suggests the presence of PANI on the MWNT-S surface, and that the unsaturated bonds in PANI do not react with sulfur during the *in situ* polymerization (EDS of the MWNT-S composite is shown in Fig. S2, ESI†).

The homogeneous core-shell structures of the MWNT-S composites give rise to their excellent electrochemical performance as cathode materials for Li-S batteries. A MWNT-S composite prepared by thermal treatment (MWNT-S-TT) was used as the control sample (see ESI† for details of sample preparation, cell fabrication and testing). As shown in Fig. 4a, the MWNT-S-TT exhibits an initial discharging capacity of 928 mA h g⁻¹ and a remaining capacity of

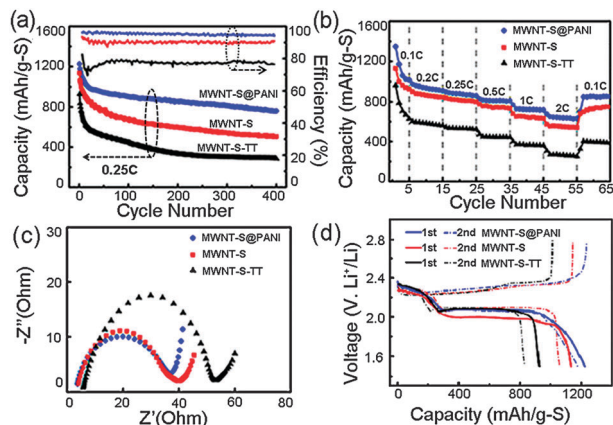


Fig. 4 Electrochemical performances of the MWNT-S, MWNT-S@PANI and MWNT-S-TT composites. (a) Cycling performance and Coulombic efficiency, (b) rate performance, (c) electrochemical impedance spectra, and (d) the discharging–charging curves.

285 mA h g⁻¹ after 400 cycles, while the Coulombic efficiencies are below 80% in cycling. The performances of MWNT-S-TTs are superior to most of the reported MWNT-S composites synthesized *via* thermal treatment,^{7,8} except that some work with a low sulfur content.⁹ In contrast, the MWNT-S exhibits a specific capacity of 1135 mA h g⁻¹ at the initial discharging process and the specific capacity remains at 505 mA h g⁻¹ after 400 cycles, while the Coulombic efficiencies are around 90%. It is the first report of MWNT-S composites with a satisfying cycle stability of >400 cycles at such heavy sulfur loading. Moreover, the MWNT-S@PANI shows an initial discharging capacity of 1225 mA h g⁻¹ and a remaining capacity of 760 mA h g⁻¹ in the 400th cycle, with Coulombic efficiencies of around 95%. The capacity decay rate from the 10th to the 400th cycle is ~0.08%, which is much better than reported MWNT-S composites wrapped with polypyrrole (PPy) or PANI with similar sulfur loading.^{6,7} In these structures, the MWNTs form the electron transport framework, and the thin and homogenous sulfur coating facilitates electron transfer to sulfur, thus enhancing its utilization. The large specific surface area of MWNTs, and the coating of a PANI layer in the case of the MWNT-S@PANI composite, help to retain/confine polysulfides from dissolving into the electrolyte, which results in favorable cycle stability and high efficiency.

Furthermore, MWNT-S and MWNT-S@PANI composites show very good rate performances. As shown in Fig. 4b, a satisfactory capacity of 592 mA h g⁻¹ is obtained for the MWNT-S composite at 2 C, and the capacity recovers to 741 mA h g⁻¹ when the current rate is reduced back to 0.1 C. The PANI coating further enhances the rate performance: the MWNT-S@PANI composite exhibits a capacity of 640 mA h g⁻¹ at 2 C and 847 mA h g⁻¹ when returned to 0.1 C. These rate performances are significantly better than the control material, the MWNT-S-TT composite, and other MWNT-S composites previously reported in the literature.^{6,7}

Fig. 4c shows electrochemical impedance spectroscopy (EIS) data for freshly prepared cells at an open circuit potential. The impedance of Li-S batteries located in the high-frequency region is regarded as the charge transfer resistance (R_{ct}) of the cell.²² The R_{ct} of the MWNT-S and MWNT-S@PANI cells is 40 Ω and 37 Ω , respectively, values which are both smaller than the 53 Ω of the MWNT-S-TT cell.

This indicates that MWNT-S composites prepared *via* the sulfur-amine chemistry method have better kinetic characteristics than MWNT-S-TT composites. The reason for such good electrical conduction is probably due to the core-shell structure, with a thin and smooth sulfur coating around the highly conducting MWNT. Further coating with a conducting PANI shell also produces a slight improvement in electrical conduction, since the conducting PANI shell provides an additional electrical conduction path.^{6,21} Similarly, the over-potential of the MWNT-S composite during the first discharging process is eliminated after coating of a PANI shell (see Fig. 4d), which is also not seen again from the second cycle, because sulfur is rearranged to form an electrochemically favorable structure during the initial charging process (the corresponding CV curves are shown in Fig. S3, ESI†).

In summary, a sulfur-amine chemistry-based method has been developed to prepare MWNT-S composites. Elemental sulfur in an amine solvent exists as polysulfide ions and radical ions. S₈ molecules can be quantitatively recovered from a sulfur-amine precursor and homogeneously deposited on MWNT surfaces. Due to the thin and uniform sulfur coating around the MWNT core, the MWNT-S composite exhibits good cycle stability as a cathode material for Li-S batteries for up to 400 cycles. Further encapsulation with conducting PANI improves the cycle stability and efficiency.

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