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Tuning the structure of three dimensional nanostructured molybdenum disulfide/nitrogen-doped carbon composite for high lithium storage

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Abstract

Molybdenum disulfide/nitrogen-doped carbon nanocomposite can afford high capacity, good rate capability and cycling stability in lithium ion batteries owing to the synergistic effect from these two components. Structure of the material has a great impact on the performance as well. In this work, MoS₂/nitrogen-doped carbon (MoS₂/C) composites have been developed by manipulating the nano-featured polypyrrole templates to guide and confine their growth. They are formed via a simple hydrothermal process combined with a subsequent annealing process. The MoS₂/nitrogen-doped carbon nanotubes (MoS₂/CNT) composite with 76% of MoS₂ exhibits an excellent performance including a high capacity of 1232 mAh g⁻¹ at a current density of 0.1 A g⁻¹, outstanding rate capability (947 mAh g⁻¹ at 2 A g⁻¹), and good cycling stability with 754 mAh g⁻¹ retained over 1000 charge/discharge cycles at a high current density of 1 A g⁻¹. This performance is much better than that MoS₂/nitrogen-doped carbon nanoparticles (MoS₂/CNP) composite. This work demonstrates the importance of introducing three-dimensional nanostructures in electrode materials to improve their electrochemical performance.

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Tuning the structure of three dimensional nanostructured molybdenum disulfide/nitrogen-doped carbon composite for high lithium storage

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Abstract

Molybdenum disulfide/nitrogen-doped carbon nanocomposite can afford high capacity, good rate capability and cycling stability in lithium ion batteries owing to the synergistic effect from these two components. The structure of this material has a great impact on the performance as well. In this work, MoS₂/nitrogen-doped carbon (MoS₂/C) composites have been developed by manipulating the nano-featured polypyrrole templates to guide and confine their growth. They are formed via a simple hydrothermal process combined with a subsequent annealing process. The MoS₂/nitrogen-doped carbon nanotubes (MoS₂/CNT) composite with 75% of MoS₂ exhibits an excellent performance including a high capacity of 1232 mAh g⁻¹ at a current density of 0.1 A

g^{-1} , outstanding rate capability (947 mAh g^{-1} at 2 A g^{-1}), and good cycling stability with 754 mAh g^{-1} retained over 1,000 charge/discharge cycles at a high current density of 1 A g^{-1} . This performance is much better than the MoS_2 /nitrogen-doped carbon nanoparticles (MoS_2/CNP) composite. This work demonstrates the importance of introducing three-dimensional nanostructures in electrode materials to improve their electrochemical performance.

Keywords: Nitrogen-doped carbon; Two-dimensional material; MoS_2 ; Lithium-ion battery; Tubular nanostructure

1. Introduction

The rapid development of daily used personalized electronic devices such as cellphones, smart watches and laptops, calls for high performance lithium-ion batteries [1]. As a representative for two-dimensional (2D) transition metal dichalcogenides (TMDs) materials, molybdenum disulfide (MoS_2) is recognized as a promising alternative anode material due to its high theoretical capacity of 670 mAh g^{-1} [2-4]. Its intrinsic large interlayer distance (0.62 nm) and high surface area facilitate easy insertion of lithium ions and easy access of electrolyte [5]. However, MoS_2 nanosheets suffer from low conductivity and aggregation as well as volume changes during the repeated intercalation/deintercalation of Li ions. All these lead to poor rate capability and poor cycling stability [6-9]. In order to overcome these drawbacks, two main effective approaches are applied: incorporation with conductive carbon materials as supports and creation of three-dimensional (3D) structures [6-9]. Introducing carbon materials can increase the conductivity as well as hinder the restacking problem of MoS_2 [7, 10, 11]. A 3D structure can offer the advantages of shortened ion diffusion path, increased surface area, and accommodating volume changes as well [12].

Among various carbon materials, nitrogen-doped carbon has attracted much attention owing to its merits of affording sufficient active sites, enhanced surface wettability, and high electrical conductivity [13, 14]. The incorporation of heteroatom nitrogen into carbon creates a disordered structure with numerous defects that benefits lithium storage [15, 16]. Combining nanostructured nitrogen-doped carbon and MoS₂ afford better electrochemical performance by harnessing their inherent merits. The nitrogen-doped carbon acts as the conductive component in the composite; thus improving the rate capability and providing additional capacity as well. The 3D nanostructure can also buffer the volume changes of MoS₂ during the charge/discharge process and suppress the restacking problems thus achieving long cycle life. The nanostructured MoS₂/C composite has demonstrated excellent electrochemical properties in lithium batteries [17, 18]. For example, a high specific capacity of 947 mAh g⁻¹ at 2 A g⁻¹ was delivered by the rose-like MoS₂/nitrogen-containing carbon/graphene hybrids [6], which was fabricated by hydrothermally growing MoS₂ on PPy coated GO nanosheets in combination with a calcination process at 800 °C. Using Fe₂O₃ nanocubes as templates, the nitrogen-doped carbon@MoS₂ nanoboxes composite [19] was prepared through the carbonization process of polydopamine, etching of templates and solvothermal growth of ultrathin MoS₂ nanosheets; this material delivered a capacity of 689 mAh g⁻¹ at a current density of 2 A g⁻¹.

Nitrogen-doped carbon can be produced via chemical vapour deposition, thermal annealing, plasma treatment and the arc-discharge method [13, 20]. Using polypyrrole (PPy) to produce nitrogen-doped carbon via a carbonization process has attracted attention because of its ease of processability, the controllable nano-scaled features such as nanoparticles, nanofibres and nanotubes [20-22]. Very recently, nitrogen-doped carbon nanotubes@MoS₂ nanosheets composite was reported, and it was produced by using PPy nanotubes as template for the growth

of MoS₂ nanosheets via a hydrothermal method coupled with an annealing process [18]. This material demonstrated a high capacity of 1040 mAh g⁻¹ at 0.2 A g⁻¹ and a capacity of 645.8 mAh g⁻¹ at 1.6 A g⁻¹ after 200 cycles. However, the effect of the ratio between nitrogen-doped carbon nanotubes and MoS₂ nanosheets on the performance was not discussed. The comparison with different nanofeatures was not mentioned either.

In this work, MoS₂ nanosheets were hydrothermally grown and anchored on nanostructured nitrogen-doped carbon by using PPy nanotubes or nanoparticles as template, followed by an annealing process. The expanded interlayer distance (0.67 nm) of MoS₂ nanosheets and the nanotube structure from PPy were both retained in the MoS₂/CNT composite. Different ratios between MoS₂ and CNT were investigated to understand the relationship between the structure and electrochemical performance. The MoS₂/CNP composite was investigated as a contrast further to confirm the structural effect on the electrochemical performance. The MoS₂/CNT composite with 75% of MoS₂ displayed an excellent performance; including high capacity, outstanding rate capability and good cycling stability.

2. Experimental

2.1 Fabrication of PPy nanotubes and PPy nanoparticles

PPy nanotubes were prepared with the assistance of a reactive template formed by the anions of azo dye methyl orange (MO) and FeCl₃ [23]. In a typical procedure, MO (147.3 mg, 0.45 mmol) was dissolved into Milli-Q water (90 ml) to form an orange solution, followed by addition of FeCl₃·6H₂O (1.22 g, 4.5 mmol). A flocculent precipitate could be observed immediately in the solution. Then pyrrole monomer (4.5 mmol) was added into the mixture and kept stirred for 1 day at room temperature. The produced black precipitates were collected by centrifugation

coupled with a rinse process with Milli-Q water and ethanol to remove the impurities until the dispersion was colourless and neutral, then freeze-dried overnight to obtain PPy nanotubes.

PPy nanoparticles were obtained by employing PVA/FeCl₃ complexes as templates and oxidant [24, 25]. A solution of PVA (polyvinyl alcohol, MW=50000, 5 wt%) was prepared by dissolving PVA into Milli-Q water at room temperature, then oxidant FeCl₃·6H₂O was added to form a viscous solution which was orange in colour. Pyrrole monomers were then introduced into the solution (0.1 mol/L) for polymerization and the reaction lasted 4 h in an ice bath. The molar ratio of oxidant to monomer was 2.5:1. The same procedures that were used for PPy nanotubes collection were followed in order to collect PPy nanoparticles except that hot water was used in the rinsing process.

2.2 . Fabrication of nano-featured MoS₂/PPy and MoS₂/C composites

The freeze-dried PPy nanotubes or PPy nanoparticles (20 mg) were re-dispersed into Milli-Q water (40 ml). After a sonication process of 2 h, Na₂MoO₄ with a designated amount was added into the dispersion and stirred for 30 min. As a sulfur source and reducing agent [26], L-cysteine (C₃H₇NO₂S) was then added (L-cysteine: Na₂MoO₄ = 2: 1, by weight) and stirred for another 10 minutes. The above mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and subjected to a hydrothermal process at 180 °C for 24 h to grow MoS₂ nanosheets on the surface of PPy, forming MoS₂/PPy composites. The products were obtained following the procedures of centrifugation, washing 3 times with water, and a final freeze-drying process. This composite was named as xMoS₂/PPy, where x is the weight ratio between MoS₂ and PPy. Neat MoS₂ nanosheets were also prepared under the same conditions as control.

The products of PPy, MoS₂ nanosheets and MoS₂/PPy composites were treated at 800 °C in a tube furnace under argon flow at a heating rate of 5 °C /min and held at this temperature for 2h. The annealed PPy nanotubes/nanoparticles, MoS₂ and xMoS₂/PPy composites were assigned as CNT/CNP, annealed MoS₂ and xMoS₂/C, respectively.

2.3 Material characterizations

The nanostructure and morphology of samples were examined using transmission electron microscopy (TEM, JEOL JEM-2200FS) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500FA). Coupled energy dispersive spectroscopy (EDS) was applied to analyze the elemental distribution. BET test was conducted using Quantachrome corporation NOVA 1000 high speed gas sorption analyzer. A hemispherical energy PHOIBOS 100/150 analyzer was used to collect the X-ray photoelectron spectroscopy (XPS) data. The Raman spectra were obtained by a confocal Raman spectrometer (Jobin Yvon HR800, Horiba) using a 632.8 nm diode laser. FTIR spectra were collected using a FT-IR spectrometer (IRpretige-21, Shimadzu) over a range of 600 to 2000 cm⁻¹. Thermogravimetric analysis (TGA) was conducted on a Pyris Diamond thermogravimetric/ differential thermal analyzer at a heating rate of 10 °C min⁻¹ in air flow.

2.4 Electrochemical measurement

The electrochemical performance of these samples as a working electrode was investigated in a 2032 coin cell coupled with a lithium foil. These cells were assembled in an argon-filled glovebox (MBrau, UNIlab Plus). The electrolyte used was 1 M LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v) (Aldrich). The working electrode was fabricated by coating a mixed slurry in N-Methyl-2-pyrrolidone (NMP) containing active

materials, carbon black and polyvinylidene fluoride (PVDF) (weight ratio of 8:1:1) onto a copper foil, and then dried in a vacuum oven at 60 °C overnight. The mass loading of active materials was in a range of 1-1.2 mg cm⁻². Cyclic voltammograms (CV) were recorded using a Solartron SI 1287 electrochemical system at a scan rate of 0.2 mV s⁻¹ over a potential range of 0.01 to 3 V (vs. Li/Li⁺). Galvanostatic charge/discharge tests were conducted using a LAND CT2001A battery test system (Wuhan Jinnuo Electronics Co. Ltd.) over the potential range of 0.005 to 3 V (vs. Li/Li⁺). Electrochemical impedance spectra (EIS) were acquired using a Gamry EIS 3000 system over a frequency range of 100 kHz to 0.01 Hz with an AC perturbation of 10 mV.

3. Results and discussion

The schematic of the procedures to synthesize nano-featured MoS₂/C composite is illustrated in Figure 1. It started with the formation of a template to nucleate and confine the growth of PPy. In the solution containing MO, amorphous FeCl₃-MO aggregates with a fibrillar structure were formed as seed template for growing PPy. As the polymerization proceeded, the templates were automatically degraded due to the reduction of iron cations, thus forming PPy with a tubular nanostructure [23]. For producing PPy nanoparticles, globule PVA/Fe³⁺ complexes were employed as oxidant and the self-assembled templates. Due to the inherently hydrophobic property of pyrrole and the steric stabilization provided by PVA, the formed pyrrole chains tended to yield spherical polymer nanoparticles [24]. These formed PPy with distinct nanostructures were used for anchoring MoS₂ nanosheets that were produced from the reaction of Na₂MoO₄ with L-cysteine. The MoS₂/C composites were obtained by carbonizing PPy through an annealing process in argon. The crystallinity degree of MoS₂ was improved as well during this annealing process [6, 27].

Figure 1. Schematic illustration of the procedures to synthesize MoS₂/C composites.

Both PPy nanotubes and CNT exhibited a tubular architecture with a diameter in the range of 100 to 200 nm (SEM images, Figure 2 a and c) with clear edges (TEM images, Figure 2 b and d). Neat MoS₂ demonstrated a flower-like layer structure on the clusters (Figure S1a, Supporting Information), and no obvious structure changes were shown after the annealing (Figure S1b, Supporting Information). The annealed MoS₂ demonstrated an expanded interlayer distance of 0.67 nm, higher than that 0.62 nm for bulk MoS₂ (Figure S1c, Supporting Information). After being subjected to a hydrothermal process, uniform flower-like patterns constructed with MoS₂ nanosheets covered the surface of PPy nanotubes (Figure 2e). Those independent tubular nanostructures were retained in the MoS₂/PPy nanotubes composite (Figure 2f, taking 2MoS₂/PPy nanotubes as an example). After the annealing process, such morphology and structure were retained (Figure 2 g-h), and the annealed MoS₂ nanosheets displayed the same expanded interlayer distance of 0.67 nm (Figure 2i). The SEM images of 1MoS₂/PPy nanotubes, 4MoS₂/PPy nanotubes and their annealed products were also collected (Figure S1 d-g, Supporting Information). 1MoS₂/PPy nanotubes composite showed a similar structure as 2MoS₂/PPy nanotubes: flower-like MoS₂ nanosheets uniformly covered the PPy nanotubes; no

structural changes could be found after the annealing. For 4MoS₂/PPy nanotubes and 4MoS₂/CNT, it is noticed that MoS₂ nanosheets not only just covered the surface of PPy nanotubes or CNT but also formed MoS₂ clusters between the tubular nanostructures due to excess amounts of MoS₂ produced. Elements C, N, Mo and S were detected in 2MoS₂/CNT with uniform distribution (Figure 2j), which evidences the formation of a hybrid structure [28]. In addition, the element oxygen was also detected, and its presence may come from organic contamination and oxidized Mo atoms [29, 30]. 2MoS₂/CNT may possess the best performance since it contained higher MoS₂ mass loading than 1MoS₂/CNT, but no MoS₂ clusters formed between the tubular nanostructures compared with 4MoS₂/CNT.

Figure 2. SEM images of PPy nanotubes (a), CNT (c), 2MoS₂/PPy nanotubes (e) and 2MoS₂/CNT (g); TEM images of PPy nanotubes (b), CNT (d), 2MoS₂/PPy nanotubes (f) and 2MoS₂/CNT (h); (i) HRTEM image of 2MoS₂/CNT; and (j) EDS mapping images of 2MoS₂/CNT.

In order to investigate the influence of nanostructures on the electrochemical performance, the 2MoS₂/C composite in the form of nanoparticles was synthesized as control. The PPy nanoparticles and CNP both displayed the same spherical nanostructures with a uniform particle size of ~150 nm (Figure 3 a-b). During the hydrothermal reaction, few-layers MoS₂ with uniform flower-like patterns were grown and completely covered the surface of PPy nanoparticles (Figure 3 c-d). After carbonization, no morphological difference was observed (Figure 3 e-f). The MoS₂ with expanded interlayer (0.67 nm) was also observed in 2MoS₂/CNP, as certified by its HRTEM image (Figure 3g). The uniform distribution of C, N, Mo and S elements in EDS mapping images verifies the formation of a hybrid structure with MoS₂ homogeneously distributed on the surface of CNP (Figure 3h) [28]. The element oxygen, possibly from organic contamination and oxidized Mo atoms, was also detected [29]. BET results showed that 2MoS₂/CNT had a specific surface area of 39.7 m² g⁻¹ higher than that 12.2 m² g⁻¹ for 2MoS₂/CNP, which can also be used to elucidate the delivered good electrochemical performance by 2MoS₂/CNT.

Figure 3. SEM images of PPy nanoparticles (a), CNP (b), 2MoS₂/PPy nanoparticles (c) and 2MoS₂/CNP (e); TEM images of 2MoS₂/PPy nanoparticles (d) and 2MoS₂/CNP (f); HRTEM image of 2MoS₂/CNP (g); and (h) EDS mapping images of 2MoS₂/CNP.

The XPS spectra of PPy, MoS₂, 2MoS₂/PPy composite and their annealed products were deconvoluted to analyze their chemical structure changes before and after the annealing process. The N1s and C1s XPS spectra of tubular composites are shown in Figure 4, while those for the particulate composites are displayed in Figure S2 (Supporting Information) together with the Mo3d and S2p XPS spectra of all samples. The peaks centred at 399.7 and 401 eV in the N1s spectra (Figure 4a, Figure S2a) are attributed to the N-H bond and -N⁺ bond, respectively [31, 32]. However, the intensity of the N-H peak had obviously decreased after experiencing the

carbonization process, due to removal of most of the hydrogen atoms. In the C1s spectra (Figure 4b, Figure S2b), three peaks around 284.5, 285.6 and 287.8 eV could be recognised as sp^2 carbon (C-C), carbon in C-N bond and C=O bond, respectively [30, 33]. The decreased intensity of C=O peak after annealing is attributed to the removal of oxygen atoms, indicating a carbonization process [30]. As for the Mo3d spectrum, four typical peaks referring to Mo^{6+} , Mo 3d_{3/2}, Mo 3d_{5/2} and S2s peaks could be found (Figure S2c) [8, 34]. The Mo^{6+} peak comes from a small portion of oxidized Mo atoms, while the Mo 3d_{3/2} and Mo 3d_{5/2} peaks match well with Mo^{4+} in MoS_2 [35]. The S2p spectrum showed two peaks around 163.4 eV and 162.1 eV (Figure S2d), which are ascribed to S2p_{1/2} and S2p_{3/2}, respectively [18]. The XPS spectra of Mo3d and S2p showed no obvious differences before and after the annealing process, evidencing the chemical stability of MoS_2 .

Figure 4. XPS N1s (a) and C1s (b) spectra of PPy nanotubes, CNT, 2MoS₂/PPy nanotubes and 2MoS₂/CNT.

Raman spectra were recorded to characterize the structure of samples. Two prominent peaks were situated at ~ 380 and 406 cm^{-1} in that for MoS_2 , annealed MoS_2 , $2\text{MoS}_2/\text{PPy}$ and $2\text{MoS}_2/\text{C}$ composites (Figure 5a; Figure S3b, Supporting Information). They are derived from MoS_2 , and can be ascribed to the E_{2g}^1 mode related with the opposite vibrations of two S atoms *versus* Mo atom, and A_{1g} mode corresponding to the out-of-plane symmetric displacements of S atoms along the c-axis, respectively [36, 37]. The interval between those two peaks increased after the annealing, indicative of the increased layers of MoS_2 nanosheets [38]. PPy, CNT, CNP, $2\text{MoS}_2/\text{PPy}$ and $2\text{MoS}_2/\text{C}$ composites all displayed two characteristic peaks of carbon at 1342.2 and 1593.1 cm^{-1} (Figure S3 a and c, Supporting Information), corresponding to the defective/disordered structure (D band) and first order scattering of E_{2g} mode (G band) [8, 10].

The chemical structure was further investigated with FTIR. A series of characteristic peaks of PPy can be identified for the samples PPy nanotubes and PPy nanoparticles (Figure 5b; Figure S3d, Supporting Information). Specifically, the peak at 1545 cm^{-1} stands for pyrrole ring vibration, whereas peaks at 1297 and 1031 cm^{-1} represent the $=\text{C}-\text{H}$ in-plane vibrations, and the peak at 1165 cm^{-1} can be assigned as the C-N stretching vibrations [39-41]. The intensity of these peaks became much weaker or even hardly identified for $2\text{MoS}_2/\text{PPy}$ composites, which may be due to the coverage with MoS_2 nanosheets [39]. All the above peaks vanished in the FTIR spectra of CNT, CNP and $2\text{MoS}_2/\text{C}$ composites, indicating the successful transformation from PPy to nitrogen-doped carbon after the annealing.

TGA was used to analyze the thermal stability and degradation of these samples (Figure 5c; Figure S3e, Supporting Information). For CNP and CNT, the weight loss over the temperature

range of 300 to 500°C represents the decomposition of nitrogen-doped carbon forming carbon dioxide. The major decomposition for annealed MoS₂ started from 360°C which was caused by the oxidation of MoS₂ to MoO₃ [8, 42]. After heating to 700°C in air flow, the weight loss of CNP, CNT, annealed MoS₂, 2MoS₂/CNP, 1MoS₂/CNT, 2MoS₂/CNT and 4MoS₂/CNT composites was 98.5%, 98.2%, 17.6%, 37.5%, 42.4%, 37.2% and 33.5%, respectively. The residue of CNT and CNP after TGA test was both less than 2%, which may be ascribed to the impurities. Thus, the loading amounts of MoS₂ were estimated to be 69%, 76% and 80% for 1MoS₂/CNT, 2MoS₂/CNT and 4MoS₂/CNT composites. As expected it was 75% for 2MoS₂/CNP, very close to the ratio of 2MoS₂/CNT. The mass loading of MoS₂ in the composites is different from the designated ones owing to the removal of hydrogen and oxygen atoms during the annealing process. It is also noticed that the content of MoS₂ in 2MoS₂/CNT and 4MoS₂/CNT are very close despite a double amount of precursor Na₂MoO₄ having been used in 4MoS₂/CNT; which may be due to the loss of loosely bound MoS₂ clusters during the repeated rinsing process.

The crystal structure of PPy, MoS₂, 2MoS₂/PPy composites and their annealed products were investigated by X-ray diffraction (Figure 5d; Figure S3f, Supporting Information). The samples CNT and CNP displayed a broad diffraction peak around 25.5°, revealing a d-spacing of 0.35 nm close to the typical d-spacing of 0.34 nm for graphite [40]. These broad diffraction peaks also demonstrate that amorphous carbon dominated in the CNT and CNP samples [40]. The XRD peaks of MoS₂ were rather broad before the calcining process due to the low crystalline degree formed via the chemical method [43]. Those peaks became much sharper after the annealing, which can be ascribed to the increased degree of crystallinity [44]. The annealed MoS₂ and 2MoS₂/C composites displayed two peaks at 13.8° and 33.3°, coincident with the typical peaks

for hexagonal-phase MoS₂ (JCPDS 37-1492). However, the peak of carbon at around 25° cannot be identified in the XRD patterns of 2MoS₂/PPy or 2MoS₂/C composites, which may be explained by the observation that PPy or CNT/CNP were completely covered by MoS₂ nanosheets [28].

Figure 5. (a) Raman spectra of MoS₂, annealed MoS₂, 2MoS₂/PPy nanotubes and 2MoS₂/CNT composites; (b) FTIR spectra of PPy nanotubes, CNT, 2MoS₂/PPy nanotubes and 2MoS₂/CNT composites; (c) TGA curves of CNT, annealed MoS₂ and MoS₂/CNT composites; (d) XRD spectra of PPy nanotubes, CNT, MoS₂, annealed MoS₂, 2MoS₂/PPy nanotubes and 2MoS₂/CNT composite.

The first three cyclic voltammograms (CV) of MoS₂/C composite were recorded at a scan rate of 0.2 mV s⁻¹ (Figure 6a; Figure S4 c-d, Supporting Information). Two obvious peaks can be recognized in the first cathodic scan. The formation process of octahedral Li_xMoS₂ contributes to the first peak ~0.95 V, deriving from the insertion of lithium ions into triangular prism MoS₂ [8, 45]. The large peak at 0.5 V can be attributed to the reduction of Li_xMoS₂ to Mo and Li₂S, and formation of a solid electrolyte interface (SEI) layer [10, 45, 46]. These two peaks vanished in the following two scans indicating that the formation of SEI layer and depletion of MoS₂ in our sample is irreversible [9, 27]. Namely, MoS₂ was transferred into a mixture of S and Mo after the first cycle. In the following two cycles, two new reduction peaks arose at 1.9 V and 1.1 V corresponding to the association of Li with S and Mo, respectively [45]. In the anodic cycles, a weak and broad peak around 1.6 V and a sharp peak at 2.35 V were detected, which can be ascribed to partial oxidation of Mo atoms and the delithiation process of Li₂S, respectively [10]. CV curves after the first scan were much stable with the same peaks, agreeing well with the following discharge-charge curves [2]. The first three consecutive CV scans were analyzed to reveal the contributed capacities from insertion and surface capacitive. Both 2MoS₂/CNT and 2MoS₂/CNP displayed a very high pseudocapacitive contribution from the surface capacitive effect (Figure S5), 78% and 70% in the first scan; 70% and 62% in the following two scans along with the vanishing of irreversible capacity (35%, 32%) related to the formation of SEI and the irreversible depletion of MoS₂ [9, 27]. Higher surface capacitive contribution for 2MoS₂/CNT compared to 2MoS₂/CNP may be attributed to its higher surface area, which also indicates a better rate capability owing to the fast lithium storage behavior at high rate [10].

The first three discharge-charge curves of 2MoS₂/CNT composite were collected at a current density of 100 mA g⁻¹ over the potential range of 0.005 to 3 V (Figure 6b). The plateaus are in

good accordance with the peaks in the CV curves. The 2MoS₂/CNT composite delivered a high initial discharge capacity of 1627 mAh g⁻¹ and a reversible capacity of 1233 mAh g⁻¹ with a Coulombic efficiency of 76%. The loss of initial capacity can be attributed to formation of SEI and the trapping of lithium ions in some defect sites or disordered structures [8, 47]. This coulombic efficiency was higher than the reported rose-like MoS₂/nitrogen-containing carbon/graphene hybrids (72.8%) [6], nitrogen-doped carbon@MoS₂ nanoboxes (59.2%) [19], and MoS₂/N-doped carbon on carbon microtubes (69%) [48], indicating an easy access of electrolyte to the 2MoS₂/CNT with a 3D tubular nanostructure.

The influence of nanostructures on the electrochemical performance was investigated by using 2MoS₂/CNP as control. As expected, this control sample displayed very similar CV and discharge-charge curves (Figure S4 a-b, Supporting Information). However, it displayed an initial capacity of 1104 mAh g⁻¹ and a reversible capacity of 850 mAh g⁻¹ (77%), much lower than that of 2MoS₂/CNT. As they had same components and contents (TGA results), the increased capacity for 2MoS₂/CNT can be attributed to the 3D tubular nanostructures that can provide large surface area for lithium storage. The merits of the 3D tubular nanostructure in 2MoS₂/CNT were also reflected in the following rate capability and cycling stability.

The rate capability of MoS₂/nitrogen-doped carbon composites was investigated at five different current densities ranging from 0.1 to 2 A g⁻¹. It was found that 2MoS₂/CNT possessed much higher capacity than 1MoS₂/CNT, 4MoS₂/CNT and 2MoS₂/CNP (Figure 6c) as well as CNT and annealed MoS₂ (Figure S4e, Supporting Information). The capacity delivered from 2MoS₂/CNT was 1232, 1162, 1091, 1030, 947 mAh g⁻¹ at a current density of 0.1, 0.2, 0.5, 1 and 2 A g⁻¹, respectively. For 2MoS₂/CNP, it was only 827, 785, 655, 459, 213 mAh g⁻¹. After the current density was reversed to 0.1 A g⁻¹, the capacity of 2MoS₂/CNT was not just fully recovered but

increased to 1307 mAh g⁻¹, while a decreased capacity of 738 mAh g⁻¹ was shown for 2MoS₂/CNP. Undoubtedly, this better electrochemical performance of 2MoS₂/CNT comes from its 3D tubular nanostructures. It is also noticed that 1MoS₂/CNT showed a lower capacity, which may be ascribed to its lower content of MoS₂. The 4MoS₂/CNT with the highest content of MoS₂ displayed a similar capacity at low current density as 1MoS₂/CNT, but much lower capacity at high current density. This poor rate performance may be attributed to the formation of MoS₂ clusters between the tubular structures, which may affect the diffusion pathways for ions. The electrochemical performance of 2MoS₂/CNT is better than or comparable to most of the reported hybrid MoS₂/C materials (Table S1, Supporting Information), such as the 850 mAh g⁻¹ at 1 A g⁻¹ from the ultrathin MoS₂/nitrogen-doped graphene nanosheets [49], 926 mAh g⁻¹ at 2 A g⁻¹ from MoS₂/nitrogen-doped carbon hybrid nanorods [7], and 645 mAh g⁻¹ at 1.5 A g⁻¹ from nitrogen-doped carbon embedded MoS₂ microspheres [50]. It is also better than the 3D N-doped carbon nanotube@MoS₂ nanosheets with approximate contents and similar fabrication method [18], which delivered a capacity of 1040 mAh g⁻¹ at 0.2 A g⁻¹ and 651 mAh g⁻¹ at 1.6 A g⁻¹.

The cycling stability of 2MoS₂/CNT and 2MoS₂/CNP samples was evaluated at a current density of 1 A g⁻¹ (Figure 6d). The 2MoS₂/CNT showed a higher capacity over the prolonged cycling process than 2MoS₂/CNP as well as annealed MoS₂ and CNT samples (Figure S4f, Supporting Information). A discharge capacity of 754 mAh g⁻¹ was delivered by 2MoS₂/CNT composite at the 1000th cycle, much higher than the capacity of 113 mAh g⁻¹, 298 mAh g⁻¹ and 257 mAh g⁻¹ for 2MoS₂/CNP, annealed MoS₂ and CNT, respectively. The capacity fading from the 1st cycle to 80th cycle can be explained by the formation of SEI layer and some lithium trapped in defect sites; while the second capacity dropping from the 200th cycle to 350th cycle may be caused by the loss of active material and electrolyte occurred under such a rigorous cycling test condition

[51]. More importantly, 2MoS₂/CNT displayed a coulombic efficiency of around 100% over the whole cycling process, indicating an outstanding cycling stability.

Figure 6. (a) The first three cyclic voltammograms of 2MoS₂/CNT composite at a scan rate of 0.2 mV s⁻¹; (b) The first three discharge/charge curves of 2MoS₂/CNT composite at a current density of 100 mA g⁻¹ over a potential range of 0.005 to 3 V; (c) Rate capability of 2MoS₂/CNP and MoS₂/CNT composites; (d) Cycling stability of 2MoS₂/CNP and 2MoS₂/CNT composite at a current density of 1 A g⁻¹.

To investigate the electrochemical impedance properties, Nyquist plots of MoS₂/CNT composites were recorded after the cycling stability test (Figure 7), which were fitted using an equivalent circuit model (Figure 7b). The slope of the line at low frequency represents the

diffusion rate of electrolyte ions, and the semicircle is related with the charge transfer resistance at the interface of electrolyte and active materials, while the intercept at high frequency is assigned as contact resistance [35]. Parameters R_s , R_{ct} , CPE and W_o used in the model represent contact resistance, charge transfer resistance, constant phase element and Warburg impedance, respectively [10, 52]. The increased slope could be attributed to the increased diffusion pathways provided by the tubular nanostructure of CNT. Nyquist plots of fresh battery cells (Figure S6) showed that 4MoS₂/CNT has the largest R_{ct} of 842 Ω compared with 617 Ω for 2MoS₂/CNT and 608 Ω for 1MoS₂/CNT, due to the extra MoS₂ clusters formed between the tubular structure. After cycling test, the charge transfer resistance was improved due to the enhanced kinetic performance upon cycling [10, 11]. The sample 1MoS₂/CNT possessed the smallest R_{ct} value, 188 Ω compared with 257 Ω for 2MoS₂/CNT and 624 Ω for 4MoS₂/CNT. The decreased amplitude of R_{ct} for these samples further verified the important function of CNT as conductive structural material. Electrochemical impedance spectroscopy of the 2MoS₂/CNT composite at different cycling numbers (Figure 7b) was also conducted to further characterize this sample by analyzing the impedance changes related with the cycling test. The R_{ct} value was 617, 355, 301, 265 and 257 Ω at 0, 10, 20, 50 and 100 cycles, respectively. The decreased charge transfer resistance well demonstrated the enhanced kinetic performance upon cycling [10, 11]. Moreover, the slopes increased with the cycling numbers, which may be attributed to the introduction of new micro-channels during cycling, thus facilitating the diffusion of electrolyte ions [8].

Figure 7. (a) Nyquist plots (symbols) and fitting curves (lines) of MoS₂/CNT composites at the open circuit potential over a frequency range of 100 kHz to 10 mHz; (b) Nyquist plots (symbols) and fitting curves (lines) of 2MoS₂/CNT composite at different cycling numbers, inset in (b) is the equivalent circuit.

4. Conclusion

Tubular MoS₂/CNT composites were synthesized by using a hydrothermal reaction with PPY nanotubes as templates coupled with a subsequent annealing process. The important role of tubular nanostructure in improving the electrochemical performance has been demonstrated by using MoS₂/CNP with same components as control. The MoS₂/CNT composite with 75% of MoS₂ affords a high capacity (1232 mAh g⁻¹ at 0.1 A g⁻¹), outstanding rate capability (947 mAh g⁻¹ at 2 A g⁻¹), and good cycling stability (754 mAh g⁻¹ after 1000 cycles at 1 A g⁻¹). This excellent electrochemical performance may be ascribed to the large interlayer distance of MoS₂, the introduced nitrogen-doped carbon component with abundant active sites and improved conductivity, as well as the created 3D tubular nanostructures facilitating ions transport. This work demonstrates a straightforward and controllable method to produce 3D nanostructures with improved electrochemical performance.

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Supporting Information

Tuning the three dimensional nanostructured molybdenum disulfide/nitrogen-doped carbon composite for high lithium storage performance

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Figure S1. SEM images of MoS₂ (a), annealed MoS₂ (b), 1MoS₂/PPy nanotubes (d), 1MoS₂/CNT (e), 4MoS₂/PPy nanotubes (f), and 4MoS₂/CNT (g); HRTEM image of annealed MoS₂ (c).

Figure S2. XPS N1s (a) and C1s (b) spectra of PPy nanoparticles, CNP, 2MoS₂/PPy nanoparticles and 2MoS₂/CNP composites; XPS Mo3d (c) and S2p (d) spectra of MoS₂, Annealed MoS₂, 2MoS₂/PPy, 2MoS₂/CNT and 2MoS₂/CNP composites.

Figure S3. (a) Raman spectra of PPy nanotubes, CNT, 2MoS₂/PPy nanotubes and 2MoS₂/CNT composites; (b-c) Raman spectra of PPy nanoparticles, CNP, 2MoS₂/PPy nanoparticles and 2MoS₂/CNP composites; FTIR spectra (d) and XRD curves (f) of PPy nanoparticles, CNP, 2MoS₂/PPy nanoparticles and 2MoS₂/CNP composites; (e) TGA curves of CNP and 2MoS₂/CNP composite.

Figure S4. The first three cyclic voltammograms of 2MoS₂/CNP (a), 1MoS₂/CNT (c) and 4MoS₂/CNT (d) composite at a scan rate of 0.2 mV s⁻¹; (b) The first three discharge/charge curves of 2MoS₂/CNP composite at a current density of 100 mA g⁻¹ over a potential range of 0.005 to 3V; Rate capability (e) and cycling stability (f) of annealed MoS₂ and CNT.

Figure S5. Bar chart displaying the capacity contributions of 2MoS₂/CNT (left column) and 2MoS₂/CNP (right column) in the first three discharge cyclic voltammograms scans.

Figure S6 Nyquist plots (symbols) and fitting curves (lines) of fresh battery cells made at the open circuit potential over a frequency range of 100 kHz to 10 mHz.

Table S1. Electrochemical performance of 2MoS₂/CNT composite prepared in this study in comparison with the reported results for MoS₂/nitrogen-doped carbon composites

Production	Electrochemical performance	Ref.
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	Capacity (mAh g ⁻¹) / current density (A g ⁻¹)	Capacity (mAh g ⁻¹) / Cycle number /Current density (A g ⁻¹)	
2MoS ₂ /CNT	1232/0.1, 947/2	754/1000/1	This work
MoS ₂ /nitrogen-containing carbon/graphene hybrids	1183/0.1, 947/2	1093/100/0.2	[1]
N-doped carbon nanotube@MoS ₂ nanosheets	1040.2/0.2, 651.2/1.6	645.8/200/1.6	[2]
C@MoS ₂ nanoboxes	1280/0.1, 689/2	952/200/0.4	[3]
MoS ₂ /nitrogen-doped carbon hybrid nanorods	1100.6/0.1, 926/2	890/100/1	[4]
MoS ₂ /Nitrogen-Doped Graphene Nanosheets	1021.2/0.1, 850/1	1285.3/50/0.1	[5]
nitrogen-doped carbon@MoS ₂	1010/0.15, 645/1.5	1055/100/0.15	[6]
carbon-coated MoS ₂ /nitrogen- doped graphene aerogel	980/0.2, 630/2	900/500/0.2	[7]
Nitrogen and sulfur co-doped graphene supported MoS ₂	1100/0.15, 860/1.5	1010/50/0.15	[8]
MoS ₂ -PPY-rGO	1085/0.2, 600/2	1070/400/0.2	[9]
core-shell C@MoS ₂ microspheres	690/0.1, 670/1	652/100/0.1	[10]
MoS ₂ /C sample	1042/0.1, 511/1	888.1/50/0.1	[11]
MoS ₂ /C hybrids	967/0.2, 353.5/1.6	400/500/1.6	[12]
MoS ₂ /C flower-like microspheres	911.6/0.2, 574.1/4	916.6/400/0.2	[13]
MoS ₂ / N-doped carbon on carbon microtubes	1090/0.2, 600/4	1058/500/0.2, 571/320/4	[14]

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