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Aligned carbon nanotube/molybdenum disulfide hybrids for effective fibrous supercapacitors and lithium ion batteries†

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An aligned carbon nanotube/MoS₂ nanosheet hybrid fiber was synthesized to display combined remarkable mechanical, electronic and electrochemical properties. It was used to fabricate flexible fibrous supercapacitors and lithium ion batteries with a high specific capacitance of 135 F cm⁻³ and a high specific capacity of 1298 mA h g⁻¹, respectively.

Introduction

The wearable electronics industry is widely recognized to be undergoing a technological revolution, the efforts of which are currently being hindered by challenges in finding suitably wearable power systems. The planar and bulky structure of conventional energy storage devices such as supercapacitors and lithium ion batteries (LIBs) cannot effectively meet the requirement to be flexible, integratable and weavable.^{1–10} To this end, a family of fibrous supercapacitors^{10–14} and LIBs^{15–17} was developed to solve this problem. However, the electrochemical performances are much lower than their planar counterparts due to the difficulty in finding appropriate fibrous electrodes that are expected to be flexible and strong with combined high electrical conductivity and electrochemical activity.^{18,19}

Fibrous electrodes were extensively constructed from aligned carbon nanotube (CNT) fibers with both remarkable electrical and mechanical properties but with intrinsically limited energy storage capabilities.²⁰ Therefore, functional components like polyaniline,²¹ MnO₂ (ref. 22) and LiMn₂O₄ (ref. 16) were incorporated to enhance the performance. The electrochemical performances of these composite electrodes were strongly dependent on the interface between the CNT and guest

component, which had an important impact on the electron transport and ion migration. CNT fibers can be hybridized with functional components through chemical and physical approaches. For instance, conducting polymers were deposited onto the surface of CNT fibers by electrochemical polymerization,² while LiMn₂O₄ particles were embraced within CNT fibers through a solution-based deposition.¹⁶ Although the effectiveness of these methods has been demonstrated, several problems still reside: first, the chemically deposited materials incline to adhere on the surface of CNT fibers and the inside is rarely accessed; second, the active materials that have been embraced in CNT fibers are weakly anchored on the CNT and are prone to agglomerate, leading to an incomplete utilization. Hence, the introduced guest components are less able to offer substantial advantages to fibrous electrodes.

Molybdenum disulfide (MoS₂) is a typical two-dimensional layered transition-metal dichalcogenide material. MoS₂ nanosheets show high energy storage capacity,^{23–25} which is widely appreciated as an alternative material for supercapacitors²⁶ and LIBs.^{4,27–29} However, due to the low conductivity of MoS₂, high electrochemical properties cannot be effectively utilized. Besides, it is difficult to synthesize single or few-layered MoS₂ nanosheets which can provide the largest surface area and are extremely useful for energy storage.^{30,31}

In this communication, an aligned CNT/MoS₂ hybrid was synthesized with few-layered MoS₂ nanosheets wound on the surface of the CNT. Here, aligned CNTs were used as templates for confining and directing the growth of MoS₂ nanosheets to form a curved structure around them. The designed hybrid nanostructure efficiently combined the superiority of high electrical conductivity in the CNT and high energy storage capacity in MoS₂, which was promising for energy storage. Both fibrous supercapacitors and LIBs were thus fabricated from the hybrid fibrous electrode to exhibit higher electrochemical performances compared with their previous planar and other fibrous counterparts.^{32–36} For instance, the specific capacitance achieved is 135 F cm⁻³ at 5 mV s⁻¹ in the fibrous supercapacitor and the specific capacity reached is 1298 mA h g⁻¹ at 0.2 A g⁻¹ in

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the fibrous LIB. Besides, both fibrous supercapacitors and LIBs were flexible and weavable, which satisfied the next-generation wearable and portable electronic devices.

Experimental section

Synthesis of the aligned CNT/MoS₂ hybrid nanostructure

Typically, 34.2 mg of poly(vinyl pyrrolidone) (M_w of 40 000) was dissolved in 70 mL of *N,N*-dimethylformamide under vigorous stirring for 1 h. Then, 137 mg of ammonium tetrathiomolybdate was added to the resulting solution, followed by an ultrasonic treatment for 2 h and vigorous stirring for 10 h to produce a homogeneous precursor solution. The precursor solution was then transferred to a Teflon-lined stainless steel autoclave (100 mL). The aligned CNT sheets that had been paved on a polytetrafluoroethylene substrate were then immersed in the precursor solution. The autoclave was heated in a muffle furnace at 220 °C for 6 h. After cooling down to room temperature, the synthesized aligned CNT/MoS₂ hybrid sheet was twisted into a fiber, followed by drying at 80 °C for 12 h.

Fabrication of fibrous supercapacitors and LIBs

Two aligned CNT/MoS₂ hybrid fibers that served as electrodes were coated with a layer of a gel electrolyte and twisted into a fibrous supercapacitor. The used gel electrolyte was prepared by dissolving 0.67 g of poly(vinyl alcohol) in 6.04 g of deionized water at 90 °C for 5 h, followed by the addition of 0.67 g of H₃PO₄. For the fibrous LIB, an aligned CNT/MoS₂ hybrid fiber was used as the cathode and paired with a lithium wire anode. The ends of the two electrodes were connected to copper wires using silver glue for further electrochemical measurement. The two electrodes were sealed in a heat-shrinkable tube with a separator between them. LiPF₆ (1 M) in a solvent mixture of ethylene carbonate, diethyl carbonate and dimethyl carbonate (weight ratios of 1 : 1 : 1) was used as the electrolyte (also called LB303), which was injected into the tube at the final step. The fabrication of the fibrous LIB was carried out in an Ar-filled glove box (MIKROUNA Super 1220/750).

Results and discussion

The synthesis of the aligned CNT/MoS₂ hybrid nanostructure is schematically illustrated in Fig. 1a. Aligned CNT sheets were dry-drawn from spinnable CNT arrays³⁷ (Fig. S1†) and then immersed in a reaction solution containing (NH₄)₂MoS₄ as a MoS₂ precursor and polyvinylpyrrolidone as a surfactant. During the solvothermal synthesis, MoS₂ nanosheets were found to be prone to grow on the outer walls of individual CNTs due to their high surface energy. Each CNT was wrapped by a layer of MoS₂ nanosheets and the MoS₂ nanosheets were then continually grown on the wrapped CNT to form an aligned hybrid nanostructure (Fig. S2 and S3†). Energy dispersive X-ray spectroscopy further shows that the CNT was uniformly wrapped with MoS₂ (Fig. S4†).

The above CNT/MoS₂ hybrid sheets were finally twisted into the hybrid fiber. The hybrid fiber showed a uniform diameter of

~65 μm (Fig. 1b). The MoS₂ nanosheets were well distributed, and the CNT remained highly aligned in the hybrid fiber (Fig. 1c and d). In other words, the MoS₂ nanosheets had been well wrapped on the aligned CNT. The high-magnification transmission electron microscopy (TEM) image showed that these aligned hybrid nanostructures were constructed from ultrathin MoS₂ nanosheets. The MoS₂ nanosheets adopted a fashion of intergrowth to support each other and interwove together into a hybrid nanostructure along the aligned CNT, preventing the aggregation of MoS₂ nanosheets (Fig. 1e). The Brunner–Emmet–Teller surface area of the hybrid fiber was calculated to be as high as 187.6 m² g⁻¹ from nitrogen adsorption–desorption isotherms (Fig. S5†). The selected-area electron diffraction pattern of the MoS₂ nanosheet revealed a typical polycrystalline structure (Fig. 1e), and it exhibited an interlayer spacing of 0.63 nm (Fig. 1f). X-ray photoelectron spectroscopy was used to investigate the chemical states of Mo and S (Fig. 1g). The binding energies of Mo 3d_{3/2}, and Mo 3d_{5/2} peaks are located at 231.8 and 228.6 eV, respectively, indicating the formation of Mo⁴⁺ in MoS₂. The binding energies of S 2p_{1/2} and S 2p_{3/2} are located at 163 and 161.6 eV, respectively, which were attributed to the S²⁻ of MoS₂.^{38,39}

The interaction between the CNT and MoS₂ in the hybrid fiber had been analyzed by Raman spectroscopy (Fig. S6†). The G band of the CNT in the aligned CNT/MoS₂ hybrid fiber was located at 1587.5 cm⁻¹.⁴⁰ Compared with the bare CNT fiber, the G band of the CNT exhibited a red-shift of 6 cm⁻¹ due to the change in the electronic structure of the CNT after wrapping with MoS₂ nanosheets.³¹ On the other hand, the MoS₂ nanosheet was well wrapped on the curved CNT even after the hybrid fiber was bent for 1000 cycles, which also verified the strong interaction between the MoS₂ nanosheet and CNT (Fig. S7†). The resistances were further traced during the bending cycles to verify the structural integrity of the hybrid fiber (Fig. S8†). The resistances were varied in less than 1% after bending for hundreds of cycles.

To fabricate a fibrous supercapacitor, two hybrid fibers were first coated with a layer of poly(vinyl alcohol)/H₃PO₄ gel electrolyte and then twisted together. The gel electrolyte also functioned as the diaphragm to prevent short circuit. The structure of the fibrous supercapacitor is schematically illustrated in Fig. 2a and the electrochemical performance was carefully tested. The cyclic voltammograms exhibited a typical rectangular shape, indicating an electrical double-layer behavior (Fig. 2b). In addition, the rectangular shape had been well maintained with increasing scan rates from 5 to 100 mV s⁻¹. A high specific capacitance of 135 F cm⁻³ was achieved at a scan rate of 5 mV s⁻¹ and was slightly decreased with the increasing scan rate (Fig. 2c). The high stability reflected by cyclic voltammetry was also verified by the galvanostatic charge–discharge profiles that maintained a triangular shape at increasing current densities from 1 to 10 A cm⁻³ (Fig. 2d). According to the discharge curves, the specific capacitance can be maintained at 92% after 10 000 charge–discharge cycles (Fig. 2e). The high rate performance and cyclic properties may be explained by the effective interaction between the MoS₂ nanosheet and CNT in the hybrid fiber.

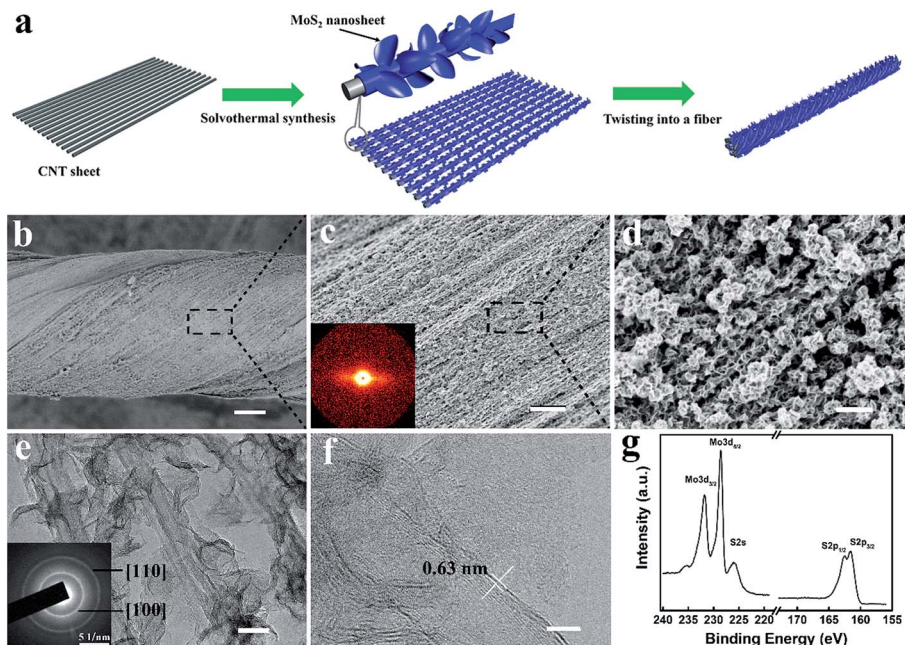


Fig. 1 (a) Schematic illustration of the synthesis of the aligned CNT/MoS₂ hybrid fiber; (b–d) SEM images of a hybrid fiber with increasing magnifications; the inserted image at (c) is the corresponding small angle X-ray scattering pattern; (e) TEM image of CNTs coated with MoS₂ nanosheets with an inserted electron diffraction pattern; (f) higher magnification of (e). (g) X-ray photoelectron spectroscopy spectrum of the aligned CNT/MoS₂ hybrid fiber. Scale bars, 15 μm (b), 2 μm (c), 0.3 μm (d), 30 nm (e) and 5 nm (f).

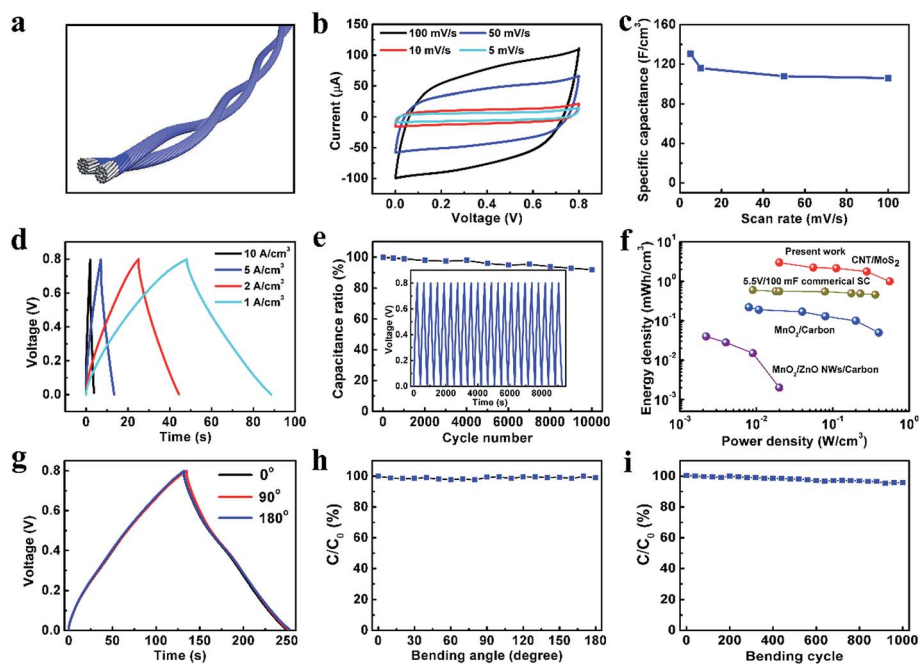


Fig. 2 Electrochemical performances of the fibrous supercapacitor twisted from two aligned CNT/MoS₂ hybrid fibers. (a) Schematic illustration of the structure of the fibrous supercapacitor. (b) Cyclic voltammograms at increasing scan rates. (c) Specific capacitances at increasing scan rates. (d) Galvanostatic charge–discharge profiles at increasing current densities. (e) Cycling performance of the supercapacitor at 1 A cm^{−2} (inserted, charge–discharge profiles). (f) Ragone plots of the present fibrous supercapacitor compared with the commercially available supercapacitor and previous fibrous supercapacitors. (g) Galvanostatic charge–discharge profiles of a fibrous supercapacitor before and after bending to 90° and 180°. (h) Dependence of specific capacitance on the bending angle. C₀ and C correspond to the specific capacitances before and after bending to different angles, respectively. (i) Dependence of specific capacitance on the bending cycle. C₀ and C correspond to the specific capacitances before and after bending to 90° for different cycles, respectively.

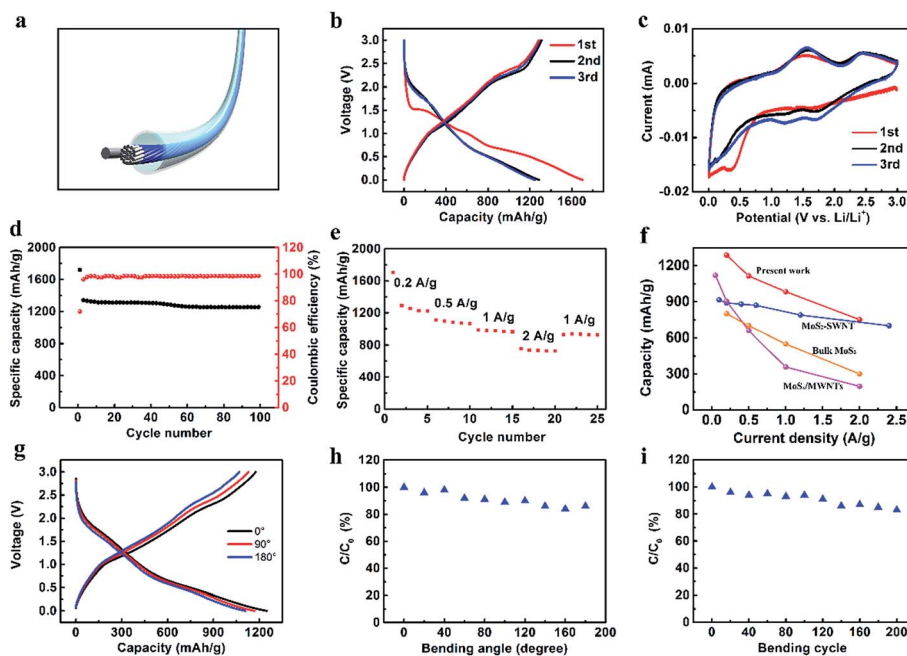


Fig. 3 Electrochemical performances of the fibrous LIB with the aligned CNT/MoS₂ hybrid fiber as the cathode. (a) Schematic illustration to the structure of the fibrous LIB. (b) The first three charge–discharge curves at 0.2 A g⁻¹. (c) Cyclic voltammograms at 0.1 mV s⁻¹. (d) Cycling performances at 0.2 A g⁻¹. (e) Rate performances. (f) Specific capacities at increasing current densities compared with previously reported MoS₂-based LIBs. (g) Galvanostatic charge–discharge curves of a fibrous LIB before and after bending to 90° and 180°. (h) Dependence of specific capacity on the bending angle. C₀ and C correspond to the specific capacities before and after bending to different angles, respectively. (i) Dependence of specific capacity on the bending cycle. C₀ and C correspond to the specific capacities before and after bending to 90° for different cycles, respectively.

The fibrous supercapacitor exhibits power densities up to $\sim 0.55 \text{ W cm}^{-3}$ and energy densities up to $\sim 3 \text{ mW h cm}^{-3}$, which outperform the commercially available supercapacitor (5.5 V 100 mF)³ and other flexible supercapacitors (Fig. 2f).^{32,33} The high performance of the CNT/MoS₂ fiber electrode is explained below. The aligned CNT fiber not only acts as a freestanding physical support but effectively functions as a conductive pathway for the rapid transport of electrons. The MoS₂ nanosheets offer high specific surface areas for charge absorption and provide large contact areas for the electrolyte. Apart from the high electrochemical performances, the CNT/MoS₂ hybrid fiber also contributed to high flexibility and deformation stability (Fig. S9†). As shown in Fig. 2g–i, the galvanostatic charge–discharge curves at increasing bending angles were perfectly overlapped and the specific capacitances were well maintained after bending to different angles. Moreover, after 1000 times of repeated bending deformations, the specific capacitance had been maintained at 95%.

Given that MoS₂ has the capability of storing lithium, the CNT/MoS₂ hybrid fiber can also serve as a fibrous cathode to produce fibrous LIBs. An aligned CNT/MoS₂ hybrid fiber and a lithium wire were assembled to fabricate a fibrous LIB (Fig. 3a). The first three charge–discharge curves at 0.2 A g⁻¹ are shown in Fig. 3b. The plateaus from the charge–discharge curves agreed with the peaks observed in the cyclic voltammograms (Fig. 3c). The fibrous LIB showed a high cycling performance, and the specific capacity was maintained above

1250 mA h g⁻¹ after 100 charge and discharge cycles (Fig. 3d). The specific capacity was calculated from the charge and discharge curves according to $C = I \times t/m$, where I , t and m correspond to the current, discharge time and mass of the cathode, respectively. Here the specific capacity was calculated from the whole electrode. The high value was derived from the high weight percentage of MoS₂ (e.g., 86%) in the hybrid fiber electrode besides the fact that no metal current collector, binder and conductive agent were used.

The CNT/MoS₂ cathode also exhibited a good rate performance (Fig. 3e). The specific capacity reached 1084 mA h g⁻¹ at 0.5 A g⁻¹, 966 mA h g⁻¹ at 1 A g⁻¹ and 720 mA h g⁻¹ at 2 A g⁻¹. Fig. 3f further compares the capacity of the present LIB with that of the reported planar MoS₂-based LIBs, and it exceeded the previous reports.^{34–36} We can conclude that the CNT/MoS₂ fiber electrodes have several advantages: it is not necessary to use a conductive agent or a metal current collector; the few layers of MoS₂ nanosheets decrease the transport distance of lithium ions, which further increases the rate of lithium insertion and deinsertion; the channels among MoS₂ nanosheet-wrapped CNTs are propitious to the infiltration of the electrolyte. The strong interaction between the MoS₂ nanosheet and CNT makes the hybrid fiber sustainable to various deformations without sacrificing performances. Similar to the fibrous supercapacitor, the fibrous LIB was also flexible and can stably work under bending and after bending for over hundreds of cycles (Fig. 3g–i).

Conclusion

In conclusion, a novel aligned CNT/MoS₂ hybrid nanostructure has been prepared to effectively combine the advantages of the CNT and MoS₂ with remarkable electrochemical performances. Both fibrous supercapacitors and LIBs are further developed from these hybrid fibers and display much higher energy storage capacities than their previous planar and fibrous counterparts. These fibrous energy storage devices are flexible and weavable and show promising applications in the next-generation wearable and portable electronic devices. This work also presents a general and effective paradigm in developing high-performance electrodes for efficient electronic devices.

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