



Tailoring the phase evolution of molybdenum-based nanocrystals in carbon nanofibers for enhanced performance of lithium-ion batteries



Tao Li ^{a,b,1}, Shouwu Gao ^{c,1}, Kun Li ^a, Guiju Liu ^d, Xiaoli Sheng ^b, Dawei Shang ^e, Limin Wu ^e, Shaojuan Chen ^a, Yiqian Wang ^{b,*}, Shaohua Wu ^{a,*}

^a College of Textile & Clothing, Qingdao University, Qingdao 266071, China

^b College of Physics, Qingdao University, Qingdao 266071, China

^c State Key Laboratory, Qingdao University, Qingdao 266071, China

^d Department of Physics, Yantai University, Yantai 264005, China

^e Qingdao Product Quality Inspection and Research Institute, Qingdao 266101, China

ARTICLE INFO

Article history:

Received 6 September 2022

Received in revised form 26 October 2022

Accepted 10 November 2022

Available online 11 November 2022

Keywords:

Nanocomposites

Electrospinning

Molybdenum nanocrystals

Carbon nanofibers

Anode materials

Lithium-ion batteries

ABSTRACT

The design and development of flexible and free-standing molybdenum (Mo)-based composite nanomaterials have aroused intensive attention in the fields of electrocatalysis, energy storage, and wearable electronics. In this study, novel nanocomposite membranes constructed with Mo-based compound nanocrystals loaded carbon nanofibers (CNFs) were successfully generated by a combination of electrospinning molybdenum acetylacetonate-contained polyacrylonitrile (PAN) solution and subsequent annealing process from 580 to 900 °C. The relationship and mechanisms between the generation of different types of Mo-based nanocrystals and the annealing temperature were systematically explored. It was found that MoO₂ nanocrystals were formed when the annealing temperature was 580 °C. With the temperature increasing, Mo₂N nanocrystals began to form due to the reaction between the formed MoO₂ and the N atoms in the PAN macromolecules. At higher temperature like 669 °C, Mo₂C nanocrystals started to form due to the reaction between Mo₂N and C atoms in the carbonized PAN macromolecules, and single-phase Mo₂C nanocrystals were produced in CNFs at 900 °C. Then, a series of flexible CNF-based nanocomposite membranes embedded with various different types of Mo-based compound nanocrystals were generated by effectively controlling the annealing temperature, which were all utilized as anodes for the construction of lithium-ion batteries. Electrochemical measurements showed that the anode materials annealed at 600 °C possessed the highest specific capacity, which were due to the high theoretical specific capacity of MoO₂ and significantly improved conductivity of Mo₂N. Moreover, all the as-developed electrodes exhibited excellent cycling stability during the charge-discharge process. The present study provides a facile and broadly-applicable routine to tailor the component, structure, and electrochemical properties of Mo-based nanocrystals in CNFs, which finds huge application potential in the fields of various flexible electrochemical devices.

© 2022 Elsevier B.V. All rights reserved.

1. Introduction

Lithium-ion batteries (LIBs) have produced a breakthrough in the energy storage field, originated from their high energy density, long life, and light weight, as well as environmental friendliness [1]. However, the currently-employed anode material (i.e., graphite) in

the commercial LIBs cannot meet the increasing demands of electronic equipment, due to their poor rate performance and low theoretical capacity [2]. To address these issues, significant efforts have devoted to the design and development of alternative anode materials. A number of recent reports have demonstrated that the nanostructured metal compounds with high energy density, long cycling life, and low cost are assuredly great candidates [3–5]. In addition, the structural limitations like poor continuity of some recently-developed electrode materials (e.g. nanoparticles, nanorods and microspheres) significantly limits the cycling stability of as-prepared LIBs. Therefore, the flexible and continuous composite

* Corresponding authors.

E-mail addresses: yqwang@qdu.edu.cn (Y. Wang),

shaohua.wu@qdu.edu.cn (S. Wu).

¹ Equal contribution to this work.

materials constructed with nanostructured metal compounds-loaded carbon-based substrates have been proposed as ideal anode alternatives most recently [6–10].

The commonly employed carbon-based flexible substrate materials include graphene, carbon nanotubes (CNTs), carbon nanofibers (CNFs), porous carbon, and carbon cloth [11–14]. In comparison, the one-dimensional (1D) CNF-constructed flexible substrates exhibit some unique advantages, such as large specific surface area, high conductivity, and excellent formability, which are all of significant importance for the fabrication of flexible LIBs with high performance [15,16]. To obtain a uniform dispersion of nanocrystals in CNFs, various preparation methods, including solvothermal synthesis [11], spray pyrolysis [15], templating [17], and electrospinning followed by thermal reduction [18], have been utilized. Compared with traditional solvothermal and template methods, electrospinning exhibits more intriguing features for the fabrication of 1D structures such as microstructure design, surface modification, control of elemental composition, and large-scale manufacturing [19,20].

When talking about the nanostructured metal compounds, molybdenum (Mo)-based compound nanocrystals possess excellent electrical, optical, and catalytic properties, which seem to be more appropriate for the construction of composite materials compared with some other transition metal-based nanocrystals like Fe_2O_3 , Co_3O_4 , CoO [21–23]. In the recent years, Mo-based compound nanocrystals/carbon composites have been widely explored to fabricate various flexible electronic devices [24–27]. Various kinds of Mo-based compounds were incorporated into CNFs by a combination of electrospinning technique and subsequent annealing at 600–900 °C [28–32]. For instance, Liu et al. directly incorporated monoclinic $\text{MoO}_{2+\delta}$ nanoparticles (~10 nm) into CNFs by electrospinning and thermal treatment at 700 °C in N_2 , yielding a reversible capacity of 876.9 mAh g^{-1} at 200 mA g^{-1} after 250 cycles when evaluated as a free-standing anode in LIBs [29]. Xiang et al. developed an anode of monoclinic MoO_2 nanoparticles/CNF membrane for LIBs using electrospinning and carbonization at 600 °C in Ar/H_2 (5:1 in volume) atmosphere, achieving a reversible capacity of 811 mAh g^{-1} at 100 mA g^{-1} after 100 cycles [30]. Li et al. prepared $\text{MoO}_2/\text{Mo}_2\text{C}$ nanocomposite/CNFs for LIBs anodes by electrospinning followed by carbonization at 800 °C in H_2/Ar (1:9 in volume) atmosphere, and delivered desirable rate capability and satisfactory cycling performance [31]. Li et al. prepared ultrafine hexagonal Mo_2C nanoparticles encapsulated in N-doped CNFs by electrospinning coupled with post-pyrolysis at 800 °C in N_2 , achieving excellent lithium storage performance when evaluated as anode for LIBs [32–34].

Unfortunately, most studies so far focused on the generation of one or two specific compounds (such as MoO_3 , MoO_2 , Mo_2C , and $\text{MoO}_2/\text{Mo}_2\text{C}$), and no systematic investigations have been reported on the relationship between the phase evolution of different types of Mo-based compounds and the annealing process with different temperatures. Worse still, the phase transformation mechanism is still unclear in the case of Mo-based compound nanocrystals embedded in CNFs. In addition, many efforts should be conducted to improve the specific capacity of Mo-based compounds by adjusting their size, crystal structure, and morphology during annealing process. In this work, we successfully realized the successful doping of different types of molybdenum (Mo)-based compound nanocrystals, including MoO_2 , $\text{MoO}_2/\text{Mo}_2\text{N}$, $\text{Mo}_2\text{N}/\text{Mo}_2\text{C}$, and Mo_2C nanocrystals, into CNFs using electrospinning technique followed by controllable high-temperature annealing in Ar atmosphere. Our results make it possible to understand the phase transformation process of Mo-based nanocrystals in the CNFs with different annealing temperatures. In addition, the obtained results indicate that the electrochemical performance of different composite membranes can be tailored by controlling the phase state of Mo-based nanocrystals in CNFs. This work provides a facile method to prepare specific Mo-based composite nanofibrous membranes, which are promising as

anode materials for the fabrication of LIBs with enhanced performance.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN, $M_w = 150,000$), molybdenum acetylacetonate [$\text{MoO}_2(\text{acac})_2$], N,N-Dimethylformamide (DMF) were purchased from the Sinopharm Chemical Reagent Co., Ltd (China). All the reagents were used as purchased without further purification.

2.2. Preparation of the Mo-based composite CNF membranes

The Mo-contained CNF composite membranes were prepared by electrospinning followed by high temperature annealing process. Firstly, the $\text{MoO}_2(\text{acac})_2$ contained PAN nanofiber membranes were fabricated by electrospinning, according to a modified procedure from previous study [35]. Specifically, PAN (9 wt%) and $\text{MoO}_2(\text{acac})_2$ (8.5 wt%) were dispersed in DMF and stirred for 2 h to form a homogeneous spinning solution. The solution was then electrospun into the nanofiber membrane (temperature: 26 °C, humidity: 33–36%, voltage: 20 kV, injection rate: 0.36 mL/h and rolling speed: 500–800 rpm). The distance was set as 16 cm from the collecting roller to the syringe needle, and the diameter of the syringe needle pinhole was 0.55 mm. After 6 h of continuous electrospinning, the as-prepared nanofiber membranes were collected and dried at 60 °C for 2–3 h. Secondly, the as-prepared nanofiber membrane was oxidatively stabilized in an oven under ambient atmosphere at 230 °C for 2 h [36–38]. Finally, the $\text{MoO}_2(\text{acac})_2/\text{PAN}$ composite nanofiber membranes were annealed at 400, 500, 580, 600, 700, 800, and 900 °C, respectively, in the Ar flow for 2 h with a heating rate of 2 °C/min, to obtain Mo-based compound nanocrystals-encapsulated CNF membranes. The samples annealed at 400, 500, 580, 600, 700, 800, and 900 °C are named as M-P 400, M-P 500, M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900, respectively.

2.3. Materials characterizations

The phases of the as-prepared CNF composites were examined using a Bruker D8 advance powder X-ray diffractometer in the 10–80° range using $\text{Cu-K}\alpha$ as radiation source ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) data were acquired using a Thermo Scientific K-Alpha+ XPS spectrometer equipped with an Al $\text{K}\alpha$ x-ray source. The morphologies were imaged using a field-emission scanning electron microscope (FE-SEM, Sigma 500). The elemental mapping of the nanofibers was carried out using an energy-dispersive X-ray spectrometer (EDS, Oxford INCAx-Sight 6427). The as-prepared composite carbon fibers were ground and dispersed in ethanol. After sonication, the dark mixture was dropped onto the Cu grid for transmission electron microscopy (TEM) imaging. TEM and high-resolution TEM (HRTEM) images were obtained by TEM (JEOL JEM2100F). High-resolution ^{13}C solid-phase nuclear magnetic resonance (NMR) spectra were recorded at 9.4 T 400 MHz NMR spectrometer operated at 400.17 MHz. The relaxation delay was 2.0 s, the acquisition time was 4.74 ms, the contact time was 2000 μs , the sweep width was 621 ppm and the number of scans was 1024. Fourier transform infrared spectroscopy (FT-IR) data were acquired using an FT-IR spectrometer (Thermo Scientific Nicolet 50, Thermo Fisher) equipped with Polaris long life infrared light source and built-in medium and far infrared diamond attenuated total reflection (ATR) module in reflectance mode. The spectral range is 4000–400 cm^{-1} with a resolution of 4 cm^{-1} . All the spectra were collected at room temperature under atmospheric pressure, with an average 60 scans for background and ATR correction.

Thermogravimetric analysis (TGA) was carried out on thermogravimetric apparatus (TG209F3, NETZSCH, Germany) at temperatures ranging from 40° to 900°C with a heating rate of 10 °C/min. The first stage was performed from 40° to 230°C under ambient air, and the second stage from 230 to 900 °C under N₂ atmosphere.

2.4. Electrochemical measurements

To evaluate the electrochemical properties of the as-prepared CNF composites, CR2025-type coin cells were assembled in a high-purity Ar-filled glove box, where the moisture and oxygen concentration is less than 0.1 ppm, using metallic lithium as a counter electrode. The as-prepared free-standing Mo-based compound nanocrystals/CNF membranes were used as anodes without any binder or conductive carbon black. The thickness of the CNF composite membranes is about 200 µm, and the mass of the composite anodes is ~0.0026 g. The electrolyte consisted of 1 M LiPF₆ solution of ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in volume).

The electrochemical performance was tested on a LAND CT2001 battery test system in the 0.01–3.00 V voltage range at room temperature. Cyclic voltammetry (CV) measurements (over the 0.01–3.00 V potential range at a scan rate of 0.1 mV s⁻¹) and electrochemical impedance spectroscopy (EIS) tests under open-circuit voltage were performed using a Metrohm Autolab electrochemical workstation (PGSTAT 302 N). The EIS tests were carried out in the 100 kHz to 0.01 Hz frequency range with a disturbance amplitude of 5 mV. Each sample was prepared more than 5 coin-cells for the electrochemical tests to determine its repeatability.

3. Results and discussion

3.1. Morphological analysis

The Mo-contained CNF composite membranes were prepared by electrospinning and followed annealing from 580 to 900 °C (Fig. 1a). Fig. S1a, c, e, and g displayed the actual photographs of as-prepared MoO₂(acac)₂/PAN composite nanofibers, pre-oxidized composite nanofibers, and Mo-contained CNFs annealed at 400–500 °C. Fig. 1b, d, f, h, and j showed the actual photographs of Mo-contained CNF composite membranes that annealed at 580–900 °C. The color of as-fabricated nanofiber composite membranes changed from light yellow to brown after pre-oxidation, then changed to black after annealing at 400–900 °C. The as-prepared and pre-oxidized nanofibers exhibited outstanding flexibility. After annealing from 400° to 900°C, the created membranes could still be easily folded without breaking, indicating that they maintained excellent flexibility after the annealing process.

Fig. S1b, d, f, and h as well as Fig. 1c, e, g, i, and k showed the representative SEM images of as-prepared MoO₂(acac)₂/PAN composite nanofibers, pre-oxidized composite nanofibers, and Mo-contained CNFs annealed at 400–900 °C. All the nanofibers possessed smooth surface morphology and were well dispersed without obvious agglomeration. The average diameter of as-prepared nanofibers was determined to be (258 ± 20) nm, and it decreased to (230 ± 16) nm after the pre-oxidation process, possibly due to the loss of water and other impurities during the pre-oxidation process. When the annealing temperature increased from 400 to 900 °C, the mean diameter of formed Mo-contained CNFs decreased from 220 ± 15–150 ± 16 nm, as shown in Fig. S2 and S3. The reduction in the nanofiber diameter was mainly attributed to the release of large amounts of non-carbon impurities, which led to the increased weight loss of nanofibers with the annealing temperature increasing [36].

3.2. Microstructure analysis

XRD patterns were acquired to investigate the crystal structure of the Mo-contained CNF composite membranes that obtained at different annealing temperatures. Fig. 2a displayed representative XRD patterns of the nanofibers that annealed at temperatures from 400 °C to 900 °C. The diffraction peaks acquired from samples M-P 400 and M-P 500 were found to be basically the same. Only two diffusive broad peaks were observed at 28° and 42°, and no other crystalline diffraction peaks were detected, indicating that the nanofibers possessed an amorphous carbon structure, which were further confirmed by TEM images (Fig. S4).

The XRD pattern of the M-P 580 showed that the amorphous phase was transformed into crystalline, as shown in Fig. 2b. The broad peak at ~26° originated from the overlap of a diffusive broad peak from amorphous carbon and a diffraction peak from the (111) plane of monoclinic MoO₂ (JCPDS no.: 65-1273). The peak at ~37° originated from the diffraction peaks from the (111), (002) and (200) planes of MoO₂. The broad peak at ~42° derived from the overlap of diffraction peaks from MoO₂. When the annealing temperature increased to 600 °C (Fig. 2c), the intensity of the peak at 43.0° (labeled by a pink circle) was enhanced in the XRD pattern, corresponding to the overlap of diffraction peaks from MoO₂ and (200) plane of Mo₂N (JCPDS no.: 75-1150). Two small peaks at 62° and 74° originated from the contribution of diffraction peaks from both monoclinic MoO₂ and tetragonal Mo₂N. When the annealing temperature increased to 700 °C, a sharp peak at 39.4° (labeled by a black diamond) started to be appeared, corresponding to the (121) plane of Mo₂C (JCPDS no.: 79-0744). The quantification analysis of the XRD pattern for M-P 600 shows that the mass ratio of MoO₂ and Mo₂N is 1:1.7.

The broad peaks of M-P 700 at ~25° and ~43° derived from the amorphous carbon and the diffraction peak from Mo₂N, respectively (Fig. 2d). The diffraction peaks at ~62.0° and ~75.4° originated from the overlap of diffraction peaks from Mo₂N and Mo₂C. When increasing the temperature to 800 °C, the XRD pattern also showed the co-existence of Mo₂C and Mo₂N (Fig. 2e), which was similar to that shown in Fig. 2d. The broad peak at ~25° originated from amorphous carbon. The increased intensity of the diffraction peak at 37.7° was ascribed to the overlap of diffraction peaks from the (200) plane of Mo₂C and the (112) plane of Mo₂N. The other two diffraction peaks at ~62.0° and ~75.4° are attributed to Mo₂C and Mo₂N. Moreover, the intensity of the diffraction peaks from the (021) and (121) planes of Mo₂C (2θ = 34.4° and 39.4°) were enhanced and the intensity of the diffraction peak at 42.7° was reduced, indicating that Mo₂N transformed into Mo₂C with the temperature increasing. In addition, with the temperature rising from 800 °C to 900 °C, the mass ratio of Mo₂N and Mo₂C goes from 1:1.4–1:1.3 by the quantification analyses of the XRD patterns. When further increasing the temperature to 900 °C, the diffraction peaks at 34.4°, 37.9°, 39.4°, 52.1°, 61.6°, 69.6°, 74.7° and 75.6°, were assigned to the (021), (200), (121), (221), (040), (321), (240) and (142) planes of Mo₂C (JCPDS no.: 79-0744), respectively, as shown in Fig. 2f. No other diffraction peaks could be detected, indicating that a single-phase of Mo₂C was formed at 900 °C.

Taken together, it could be concluded that MoO₂ was generated when the nanofibers were annealed at 580 °C. With increasing the annealing temperature, Mo₂N began to be appeared because N atoms preferentially bind to Mo atoms. This could be attributed to the high N content (26.4%) in polyacrylonitrile (PAN) and higher electronegativity of N atoms compared to C atoms [39]. When further increasing the annealing temperature, the N atoms were eliminated as N₂ and the Mo₂N started to convert into Mo₂C, leading to the co-existence of Mo₂C and Mo₂N in the created CNFs. Until the annealing temperature reached to 900 °C, a single phase of Mo₂C was obtained.

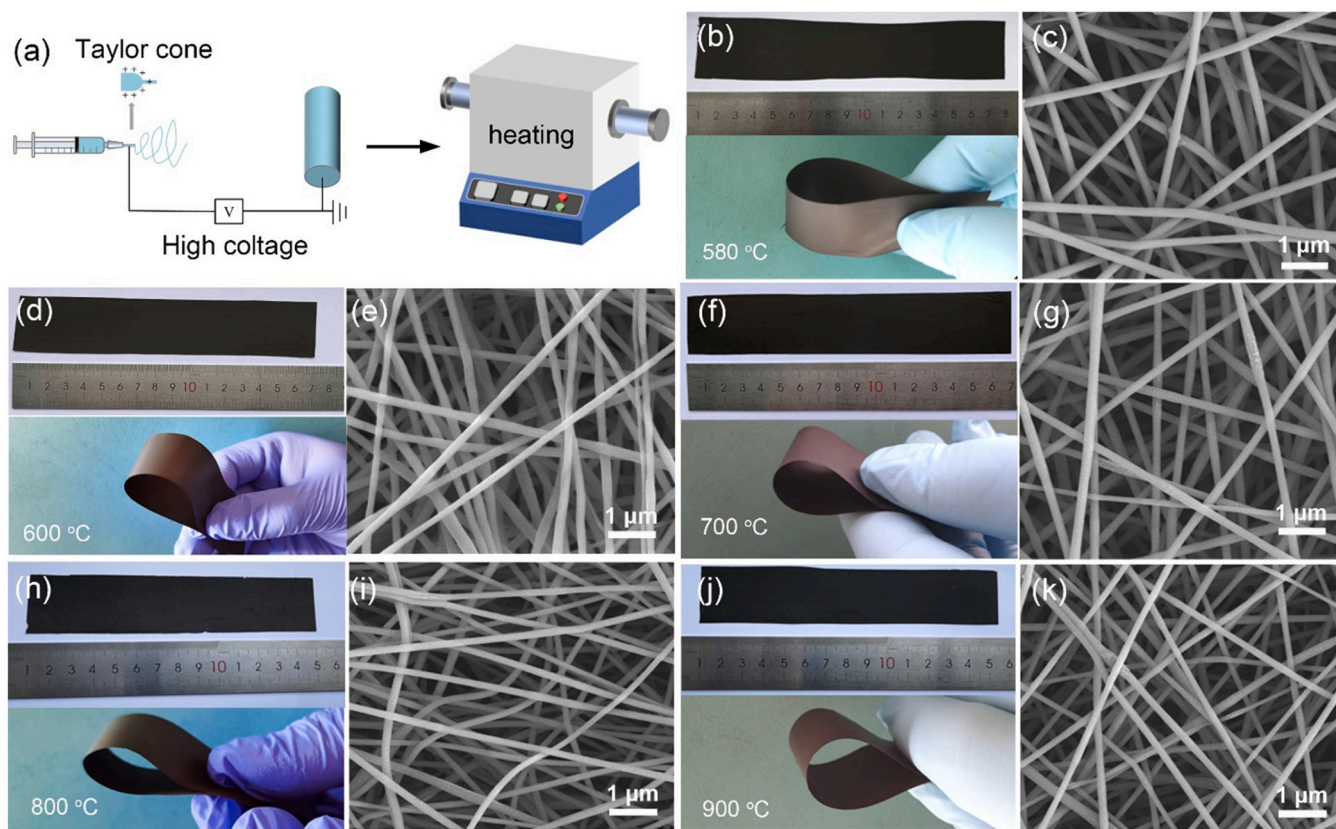


Fig. 1. The preparation process, photographs and SEM images of CNFs that annealed at 580–900 °C. (a) Preparation process of Mo-contained CNFs. Photographs of (b) M-P 580, (d) M-P 600, (f) M-P 700, (h) M-P 800, and (j) M-P 900. SEM images of (c) M-P 580, (e) M-P 600, (g) M-P 700, (i) M-P 800 and (k) M-P 900, respectively.

Extensive TEM characterizations were carried out to observe the morphology and microstructure of Mo-contained CNF composite membranes annealed at different temperatures. Fig. 3a, c, e, and g displayed the representative bright-field (BF) TEM images of M-P 580, 600, 800, and 900, and Fig. S5a showed a representative BF TEM image of M-P 700. The fibrous segments of as-synthesized samples showed relatively uniform rod-like shape with the diameters reduction from 200 to 150 nm, consistent with the SEM micrographs displayed in Fig. 1. In addition, many nanocrystals were dispersed in the prepared CNFs. Fig. 3a and c indicated that for the samples of M-P 580 and 600, the boundary of adjacent particles was not clear and the particles with a slender line-like shape were uniformly distributed in the nanofibers. When the annealing temperature increased to 700 °C, the nanocrystals were mainly located in the center of the nanofibers (Fig. S5a). As the temperature increased to 800 °C, the nanocrystals diffused outward and were uniformly distributed across the whole nanofibers. For the M-P 900, some nanocrystals diffused to the surface of the nanofibers, which was mainly ascribed to the increase of the annealing temperature. During electrospinning, the surface tension of the polymer was larger than metal salt [39], so the metallic compound nanoparticles were mainly distributed in the center of the nanofibers at a low temperature. With the temperature increasing, the thermal vibration was enhanced and the particles could easily overcome the binding energy and diffuse to adjacent regions. In other words, high temperature could supply sufficient energy for the diffusion of nanoparticles.

HRTEM was used to further clarify the microstructure of these nanocrystals. Through careful examination of more than 100 nanoparticles, only the MoO_2 phase was found in the M-P 580. Fig. 3b showed a representative HRTEM image of M-P 580 with MoO_2 nanocrystals that embedded in a CNF, in which the three particles were labeled as I, II and III, respectively. The outer part of particle I was

amorphous, demonstrating that it was not fully crystallized at 580 °C. Particle II showed a fully-crystallized structure with evident crystal lattices. The measured lattice spacing of 2.17 Å corresponded to the (210) plane of monoclinic MoO_2 (labeled by two red lines). The different crystallization state of these two nanoparticles indicated that the temperature increasing was conducive to the crystallization of the particles. The atomic plane bending (labeled by red lines) of MoO_2 in particle III took place in some regions. The lattice bending might be caused by strain during the crystallization process.

Fig. 3d displayed a representative HRTEM image of the M-P 600. The lattice spacings of the two crystal planes with an angle of 90° were measured to be 2.15 Å and 2.16 Å, corresponding to the ($\bar{2}$ 12) and ($\bar{1}$ 21) planes of MoO_2 , respectively. In addition to MoO_2 , another crystalline phase was observed in the region marked by green dotted lines in Fig. 3d. The lattice spacing of 2.10 Å was in good agreement with the (200) plane of Mo_2N (labeled by two green lines), which proved that part of MoO_2 transforms into Mo_2N when the annealing temperature reached to 600 °C. Different from the traditional process to prepare Mo_2N by calcinating MoO_x in NH_3 or H_2/N_2 atmosphere [41,42], the elemental N in our case originated from the decomposition of PAN fibers during the calcination process. Fig. S5b showed a representative HRTEM image of M-P 700, which consisted of two different kinds of nanoparticles, the upper one being Mo_2C and the lower one being Mo_2N . The lattice spacing of 2.13 Å corresponded to the (112) plane of Mo_2C . The lattice fringes with interplanar spacing of 2.00 Å corresponded to the (004) plane of orthorhombic Mo_2N . This value was in good agreement with the XRD results in Fig. 2d, which indicated that Mo_2N and Mo_2C co-existed in M-P 700.

Fig. 3f showed a representative HRTEM image of M-P 800. Similar to Fig. S5b, both Mo_2C (labeled by yellow lines) and Mo_2N (labeled by green lines) nanoparticles existed in the nanofibers. The lattice

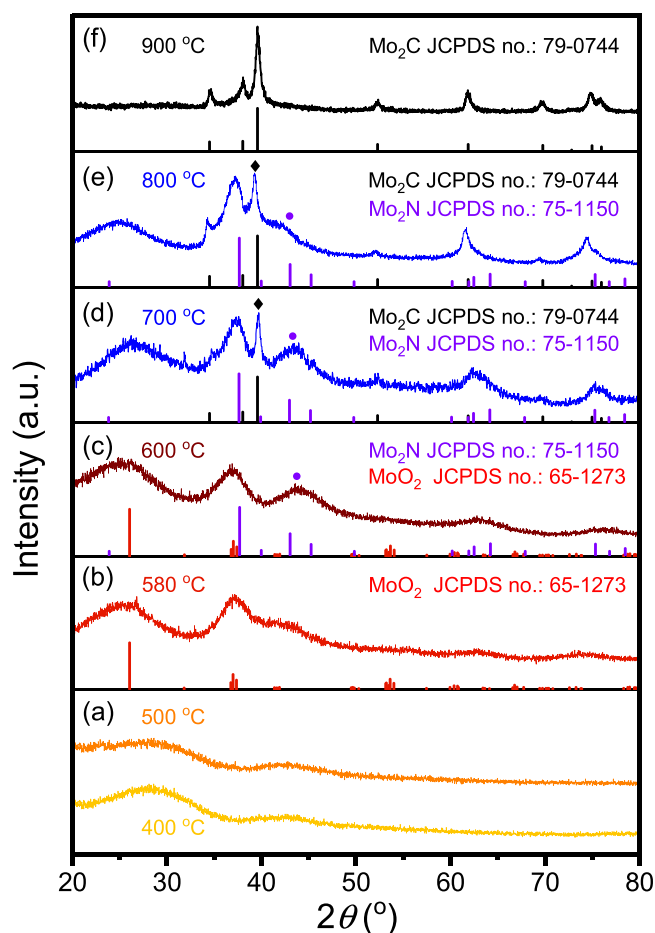


Fig. 2. XRD patterns of the composite membranes annealed at different temperatures.

spacings of the two planes with an angle of 54° were measured to be 2.02 Å and 2.13 Å, corresponding to the (2 $\bar{1}$ 1) and (112) planes of Mo₂C, respectively. In addition, the lattice spacing of 2.38 Å

corresponded to the (112) plane of Mo₂N. Compared to M-P 700, more Mo₂N nanoparticles transformed into Mo₂C when the annealing temperature increased to 800 °C. Fig. 3h showed a representative HRTEM image of the M-P 900. The lattice spacings of the two planes with an angle of 83° were measured to be 2.28 Å and 2.13 Å, corresponding to the (121) and (1 $\bar{1}$ 2) planes of Mo₂C, respectively. In addition, the lattice spacing of 2.36 Å corresponded to the (200) plane of Mo₂C. Extensive HRTEM imaging showed that only Mo₂C nanoparticles were found, indicating that all the Mo₂N were carbonized and transformed into Mo₂C, which was consistent with the XRD result of the M-P 900 (Fig. 2f).

3.3. Phase evolution process

XPS technique was acquired to analyze the change of composition and chemical bonding of Mo cations during the annealing process. All the Mo 3d spectra could be fitted using three pairs of Mo 3d ($3d_{5/2}$ and $3d_{3/2}$) with different valence states (Fig. 4). The green peaks located at 232.5 ± 0.2 and 235.6 ± 0.2 eV were attributed to the Mo (VI) $3d_{5/2}$ and Mo (VI) $3d_{3/2}$, respectively. The pink peaks located at 230.3 ± 0.6 and 233.7 ± 0.6 eV were assigned to the Mo (IV) $3d_{5/2}$ and Mo (IV) $3d_{3/2}$, respectively. The double peaks at 228.8 ± 0.5 eV and 232.2 ± 0.5 eV were attributed to the Mo (II) $3d_{5/2}$ and Mo (II) $3d_{3/2}$, respectively. Since the Mo-based CNFs were easily susceptible to surface oxidation when exposed to air, it was difficult to determine whether Mo (VI), Mo (IV), and Mo (II) originated from the nanofiber itself or from surface oxidation.

The EDS mapping were combined with the Ar⁺-etching-XPS to identify the origin of different valence states of Mo. Fig. 4a–d showed that the peak at ~ 228.8 eV was very weak, indicating that there was a small amount of Mo (II). The high-resolution XPS spectra of C 1s (Fig. S6) showed that for the M-P 500, M-P 580, and M-P 600, the C 1s peak could be fitted by C–C, C–O, C=O, and π - π^* bonds, while the Mo–C bonds began to appear when the annealing temperature reached to 700 °C. We suggested that the Mo (II) 3d peaks for M-P 500, M-P 580, and M-P 600 originated from the surface oxidation of Mo-based compounds, while for M-P 700, the Mo (II) 3d peaks derived from surface oxidation, Mo₂C, and Mo₂N, indicating the formation of Mo₂C and Mo₂N at higher annealing temperature, which

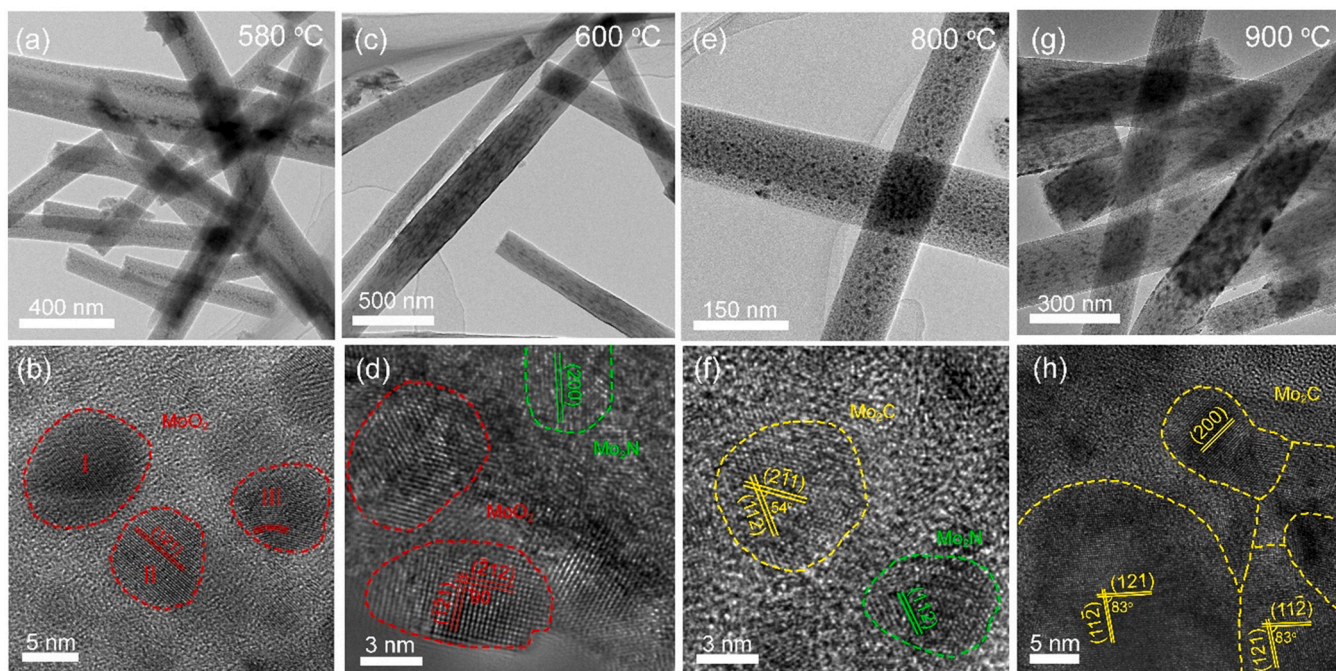


Fig. 3. Representative BF TEM and HRTEM images of the nanofibers annealed at different temperatures. (a,b) M-P 580, (c,d) M-P 600, (e,f) M-P 800, and (g,h) M-P 900.

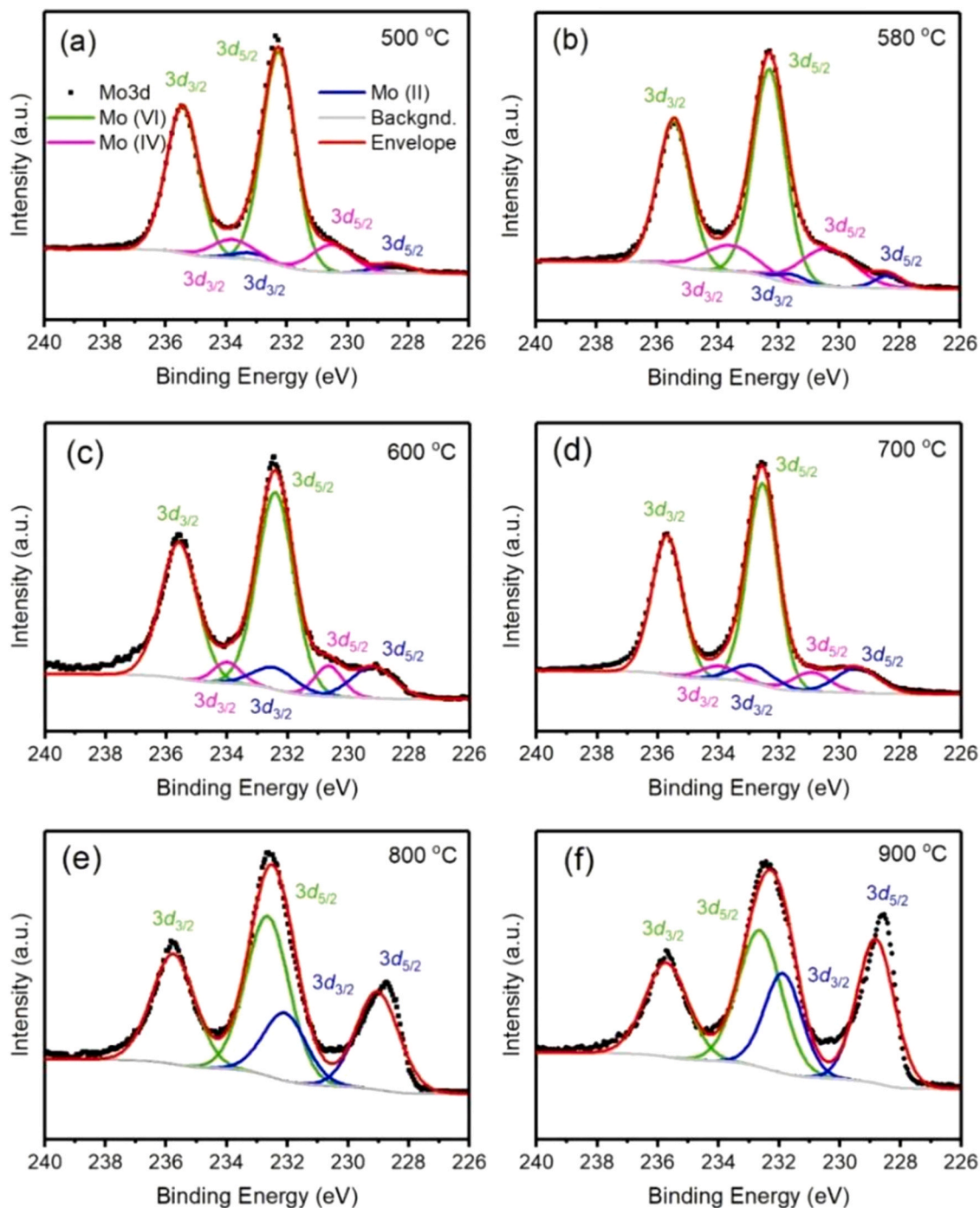


Fig. 4. High-resolution XPS spectra of Mo 3d for the nanofibers annealed at different temperatures: (a) 500, (b) 580, (c) 600, (d) 700, (e) 800, and (f) 900 °C.

was consistent with the XRD pattern (Fig. 2d). When the temperature was further increased to 800 and 900 °C, the peak profile at ~228.8 eV was obviously enhanced, indicating that the amount of Mo₂C increases significantly. In addition, the high-resolution XPS spectra of C 1s confirmed the formation of Mo-C bonds in the composites annealed at higher temperatures (Fig. S6). The peaks from MoO₃ were observed in the XRD patterns of the nanofibers annealed at temperatures of 580 °C (Fig. 2b), indicating that the Mo(IV) 3d peaks derived from both the nanofiber itself and surface oxidation, and the Mo(VI) 3d peaks originated from surface oxidation. However, when the temperature was increased to 700, 800, and 900 °C, no diffraction peaks of MoO₃ could be observed in the XRD patterns, indicating that the appearance of amorphous MoO₃ on the

nanofiber surface resulted in the Mo(VI) 3d peaks, since XPS had limited depth resolution (less than 10 nm in depth).

The amorphous nature of MoO₃ could be identified by the Ar⁺-etching XPS. Taking the M-P 800 as an example, with the increase of etching time (from 0 s to 60 s), the profile intensity of Mo(VI) 3d peaks decreased, while the profile intensity of Mo(II) 3d peaks increased (Fig. S7 and Table S1), indicating that the surface oxidation led to the formation of Mo(VI) 3d peaks. The surface oxidation phenomenon could be further probed by EDS mapping, as shown in Fig. S8. The element of Mo, O and C were uniformly distributed within the nanofibers. Moreover, the elemental O was more sparsely distributed in the nanofiber than the other elements (Mo and C), which confirmed the presence of oxygen on the surface of the

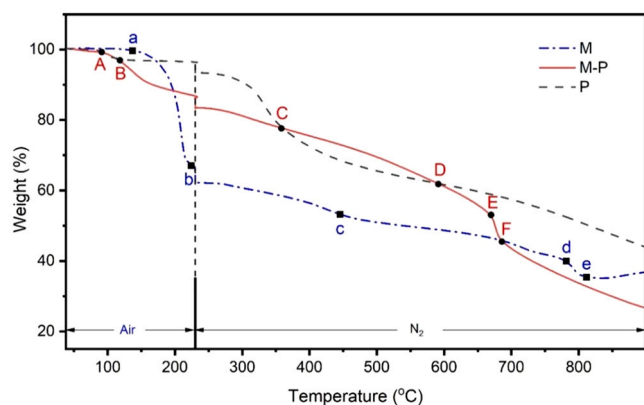


Fig. 5. TGA curves of $\text{MoO}_2(\text{acac})_2$ (M), nanofibers (M-P) and PAN membrane (P) pre-oxidized at 230 °C for 2 h in air and then annealed at different temperatures in N_2 .

nanofibers. According to the above analysis, it could be concluded that with increasing temperature, except for surface oxidation, the valence states of Mo in the nanofibers changed from Mo (VI) to Mo (IV), and Mo (II), corresponding to the evolution of Mo-based compounds from raw material, $\text{MoO}_2(\text{acac})_2$, to MoO_2 and Mo_2C .

Fig. 5 showed the TGA curves of the $\text{MoO}_2(\text{acac})_2$, nanofibers and PAN in the 40–900 °C temperature range, labeled as M, M-P, and P, respectively. For the thermal treatment process, the temperature was first increased to 230 °C in air and maintained for 2 h, then raised to 900 °C in N_2 atmosphere with a heating rate of 10 °C/min. Fig. S9 showed a representative TGA curve of $\text{MoO}_2(\text{acac})_2$ (named as M/A) heated to 900 °C in air. The TGA curve of M was presented in both Fig. S9 and Fig. 5 for comparison. The TGA curve of M/A in Fig. S9 showed that a severe weight loss of 33.5% occurred in the 136–225 °C temperature range (a' to b'), which indicated that $\text{MoO}_2(\text{acac})_2$ thermally decomposes in air. This decomposition was confirmed by FT-IR and NMR measurements, as shown in Fig. S10–14.

Fig. S10 showed representative FT-IR spectra of $\text{MoO}_2(\text{acac})_2$ before and after pyrolysis at 225 °C in air. Compared with pure $\text{MoO}_2(\text{acac})_2$, the FT-IR spectrum showed slight changes at wavenumbers of 972 cm^{-1} and 720 cm^{-1} after pyrolysis, which corresponded to the $-\text{Mo}=\text{O}$ bond and $-\text{C}=\text{C}-\pi$ bond, respectively. The generation of the $-\text{Mo}=\text{O}$ and $-\text{C}=\text{C}-\pi$ bonds was accompanied by the changes of *acac* ligands in $\text{MoO}_2(\text{acac})_2$. Certain hydrogen atoms of the $=\text{C}-\text{H}$ moieties in *acac* ligands were lost from the Mo complex to form a new $-\text{C}=\text{C}-\pi$ bond, while oxygen atoms of the carboxyl group ($-\text{C}=\text{O}$) in *acac* ligands were coordinated with Mo to create a new $-\text{Mo}=\text{O}$ bond. NMR spectra (Fig. S11–14) of $\text{MoO}_2(\text{acac})_2$ showed that in the thermal decomposition process, the number of organic $-\text{CH}_3$, $-\text{CH}$ moieties in *acac* ligands decreased due to the pyrolysis of *acac* ligands, and the amount of the $-\text{C}=\text{O}$ moieties in *acac* ligands slightly decreased due to the tight complexation between the $-\text{C}=\text{O}$ moiety and $-\text{MoO}_x$. Most probably, in this temperature range, the $-\text{CH}_3$ and $-\text{CH}$ groups were reduced and dehydrogenated, meanwhile the $\text{Mo}-\text{O}$ was crosslinked to form $\text{MoO}_x(\text{OCH}_y)_z$ [43,44].

The TGA curves of M in Fig. 5 and Fig. S9 were consistent with the curve of M/A in Fig. S9 before 447 °C (point c), except for the weight loss differences at 230 °C, indicating that the pyrolysis reactions of M and M/A were similar before 447 °C. When the temperature increased to 500 °C, $\text{MoO}_2(\text{acac})_2$ converted to MoO_3 in air, as inferred from the XRD pattern displayed in Fig. S15. The TGA curve of M in N_2 atmosphere didn't show accelerated weight loss at the temperatures from 447 °C to 500 °C, due to the absence of oxygen in the N_2 atmosphere. The decomposition/cross-linking products of $\text{MoO}_x(\text{OCH}_y)_z$ couldn't be rapidly and fully oxidized to form MoO_3 at this temperature. When further increasing the temperature, Mo_2N and Mo_2C

were gradually formed in N_2 atmosphere, as revealed by the XRD patterns shown in Fig. S16. When the annealing temperature increased to 700 °C in N_2 , the XRD pattern showed the co-existence of Mo_2N and Mo_2C (Fig. S16). When further increasing the temperature, Mo_2N gradually disappeared and the content of Mo_2C increased, which was accompanied by a further weight loss in the TGA curve of M (from point d to e in Fig. 5 and Fig. S9). The rapid weight loss was attributed to the transformation from Mo_2N to Mo_2C at 780–815 °C.

The TGA curve of P (PAN) shown in Fig. 5 was similar to previously reported observations [36,41,42]. Briefly, the PAN fibers started to lose weight at 93 °C (point A), and a small weight loss was found before 230 °C due to the dehydrogenation and transformation of the PAN polymer chain into a ladder polymer by converting the $\text{C}\equiv\text{N}$ to $\text{C}=\text{N}$ bonds. The NMR spectra of PAN treated at 225 °C (Fig. S17) showed that the amount of $-\text{CH}_3$ and $-\text{CN}$ functional groups in the PAN chains decreased, further confirming dehydrogenation and transformation of $\text{C}\equiv\text{N}$ bonds. Further weight loss in PAN was mainly caused by volatile by-products, such as methane (CH_4), hydrogen (H_2), hydrogen cyanide (HCN), water (H_2O), and CO_2 [36].

The TGA curve of the M-P displayed in Fig. 5 simulated the annealing process of the carbon flexible film loaded with molybdenum compound nanocrystals. Compared with the curves of M and P, the curve of M-P started to lose weight from 93 °C to 117 °C (point A to B) due to the decomposition of PAN. Subsequently, a rapid weight loss from 117 to 230 °C in the curve of M-P indicated the thermal decomposition of $\text{MoO}_2(\text{acac})_2$. When the temperature increased to 360 °C, the curve of M-P decreased more slowly than that of P, which was mainly due to the formation of the complex between $\text{MoO}_x(\text{OCH}_y)_z$ and PAN. From 669 to 685 °C (point E to F), the curve of M-P showed a rapid weight loss, corresponding to the formation of Mo_2C . This was further confirmed by the XRD patterns acquired at 700 °C (Fig. 2d). With further temperature increasing, the curve of M-P gradually became parallel to that of P, and the weight loss was mainly caused by the PAN carbonization and the transformation from Mo_2N to Mo_2C . When the temperature increased to 900 °C, all of the Mo_2N transformed into Mo_2C , as confirmed by the XRD patterns of Fig. 2f.

Based on the above results, we proposed a formation mechanism of the composite nanofibers. As shown in Fig. 6, the compound $\text{MoO}_2(\text{acac})_2$ began to decompose at 117 °C. It underwent dehydrogenation, $\text{Mo}-\text{O}$ crosslinking and other decomposition reactions from 117 to 500 °C, yet no crystalline nanostructures were observed within this temperature range. When the temperature exceeded 500 °C, crystalline MoO_2 nanostructures began to form. Once the temperature was higher than 580 °C, the formed MoO_2 could react with N atoms in the surrounding PAN to form Mo_2N due to the larger electronegativity of atomic N compared to atomic C [40]. Usually, Mo_2N was produced by the calcination of MoO_x in a reducing atmosphere of NH_3 or H_2/N_2 [41,42]. However, in our case, the nitrogen content of PAN was about 26.4% [40], which could provide a sufficient source of nitrogen. The MoO_2 nanocrystals exhibited a high surface area and high activity due to their small sizes, which facilitated the reaction with the surrounding nitrogen sources in the PAN. Therefore, MoO_2 nanocrystals could be transformed into Mo_2N at a high temperature even without a reducing atmosphere. Further increasing the temperature led to the formation of Mo_2C . Similar to Mo_2N , MoO_x was usually carbonized to produce Mo_2C by a reductive carbon-containing gas stream (e.g. CH_4/H_2 or CO/H_2) [45,46]. In addition, the Mo_2C could also be obtained by carbonization of Mo_2N under CO atmosphere [41]. In this case, when the annealing temperature was 700–800 °C, no MoO_x but Mo_2N was found; however, when the temperature was maintained at 900 °C for 2 h, all the Mo_2N nanocrystals were transformed into Mo_2C due to the reaction between Mo_2N and C in CNFs. We therefore confirmed that Mo_2C was formed by the conversion of Mo_2N .

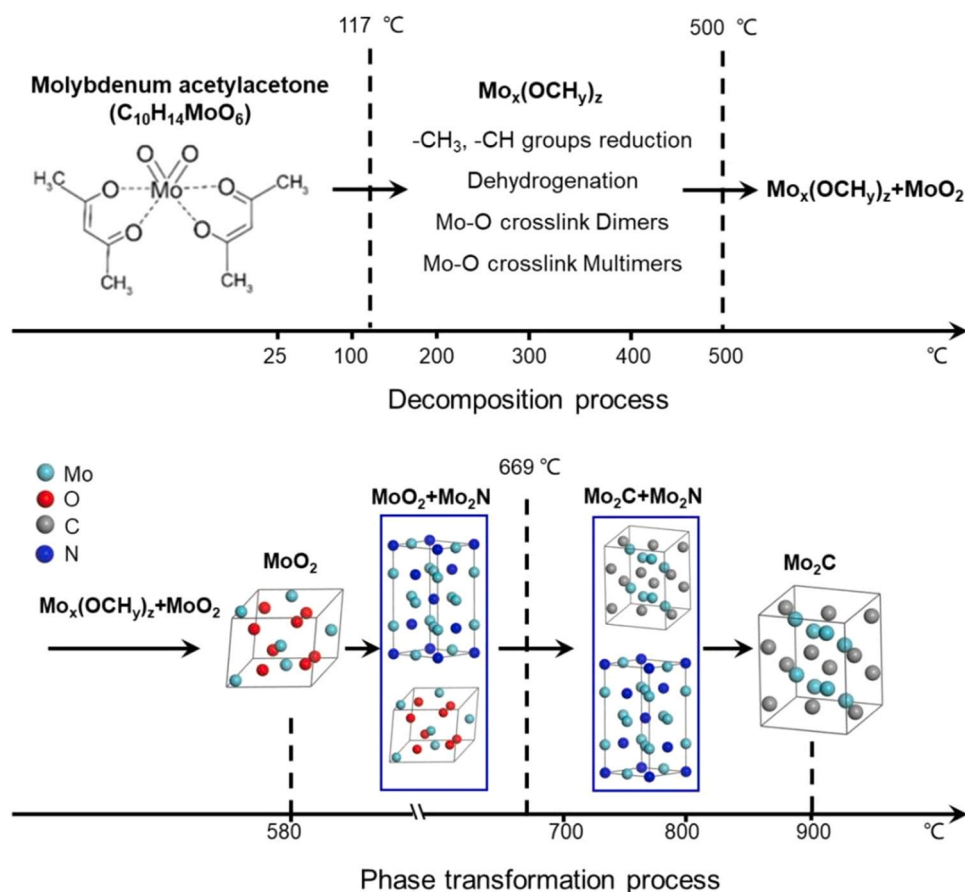


Fig. 6. Schematic diagram for the evolution of Mo-based nanostructures at different temperatures.

3.4. Electrochemical properties

To explore the electrochemical properties of the Mo-based composite CNFs, we assembled LIBs using the CNF-based membranes as anode and studied the Li-ion storage properties. For the M-P 400 and M-P 500, the annealing of $MoO_2(acac)_2$ in the fibers did not yield crystalline Mo compound particles, and the electrodes made of the M-P 400 and M-P 500 did not work properly due to the low conductivity and specific capacity. Therefore, we only investigated the electrochemical properties employing the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900 as electrodes, respectively.

Fig. S18 and Fig. 7a showed the first three and the third cycle CV curves of these five electrodes at a scan rate of 0.3 mV s^{-1} in the 0.01–3.00 V potential range, respectively. For the M-P 580 electrode, the peak located at around 0.4 V was observed in the first cycle, which was attributed to the solid electrolyte interphase (SEI) film formed by electrolyte decomposition (Fig. S18a). The CV curve did not overlap in the subsequent cycles, suggesting the formation of the SEI film and the irreversible insertion of Li^+ ions into the nanofibers, which usually caused a loss in capacity in the first discharge-charge process. Similarly, the CV curves of the M-P 600, M-P 700, M-P 800, and M-P 900 electrodes also indicated the formation of the SEI film and the irreversible insertion of Li^+ ions (Fig. S18b–e). The CV curves of the M-P 580 and M-P 600 shown in Fig. 7a indicated that two redox couples were located at 0.95/1.50 V and 1.00/1.55 V, respectively. The two reduction peaks could be ascribed to a phase transition from the orthorhombic to the monoclinic phase due to the Li insertion. The two oxidation peaks could be assigned to the phase transitions from the monoclinic to the orthorhombic phase and from the orthorhombic to the monoclinic phases in the Li extraction process, respectively [47–49]. No obvious redox peaks were found

for Mo_2C or Mo_2N in the CV curve of M-P 700, which was attributed to the low content of Mo_2C or Mo_2N that forms at 700 °C. However, the electric conductivity of the M-P 700 electrode was enhanced, thanks to the introduction of Mo_2N and Mo_2C [50]. In addition, a pair of redox peaks was located at around 1.02/1.20 V in the CV curve of M-P 800, which might correspond to the conversion or alloying reaction of Li^+ in the Mo_2C electrode [51]. The redox peaks of Mo_2N were not clearly visible in the CV curve. This might be due to the peak broadening or the low content of Mo_2N in the electrode. Similarly, a pair of redox peaks at around 1.06/1.12 V was found in the CV curve of the M-P 900, which was related to conversion or alloying reaction of Li^+ in Mo_2C .

Fig. 7b showed the charge-discharge curves of the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900 electrodes at a current density of 100 mA g^{-1} . The initial discharge capacities of the five electrodes were 699, 1057, 685, 488, and 442 mAh g^{-1} , and the initial charge capacities were 447, 832, 515, 299, and 229 mAh g^{-1} , respectively. Thus, the initial Coulombic efficiencies of the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900 electrodes were estimated as 63.9%, 78.7%, 75.2%, 61.3%, and 51.8%, respectively. The initial capacity loss might result from the incomplete conversion reaction as well as the formation of the SEI layer. Fig. S19 showed that from the second cycle, the discharge curves of M-P 600, M-P 700, M-P 800 and M-P 900 electrodes remained almost unchanged, indicating high reversibility of the lithiation/delithiation process and good stability of the four electrodes. However, for the M-P 580 electrode, the discharge curve still changed, which might be due to the low crystallinity of the nanoparticles in the nanofibers at low annealing temperatures.

To evaluate the rate performance of the five different samples, we measured the rate capacity of the molybdenum-based nanofiber electrodes at different current densities, as shown in Fig. 7c. The

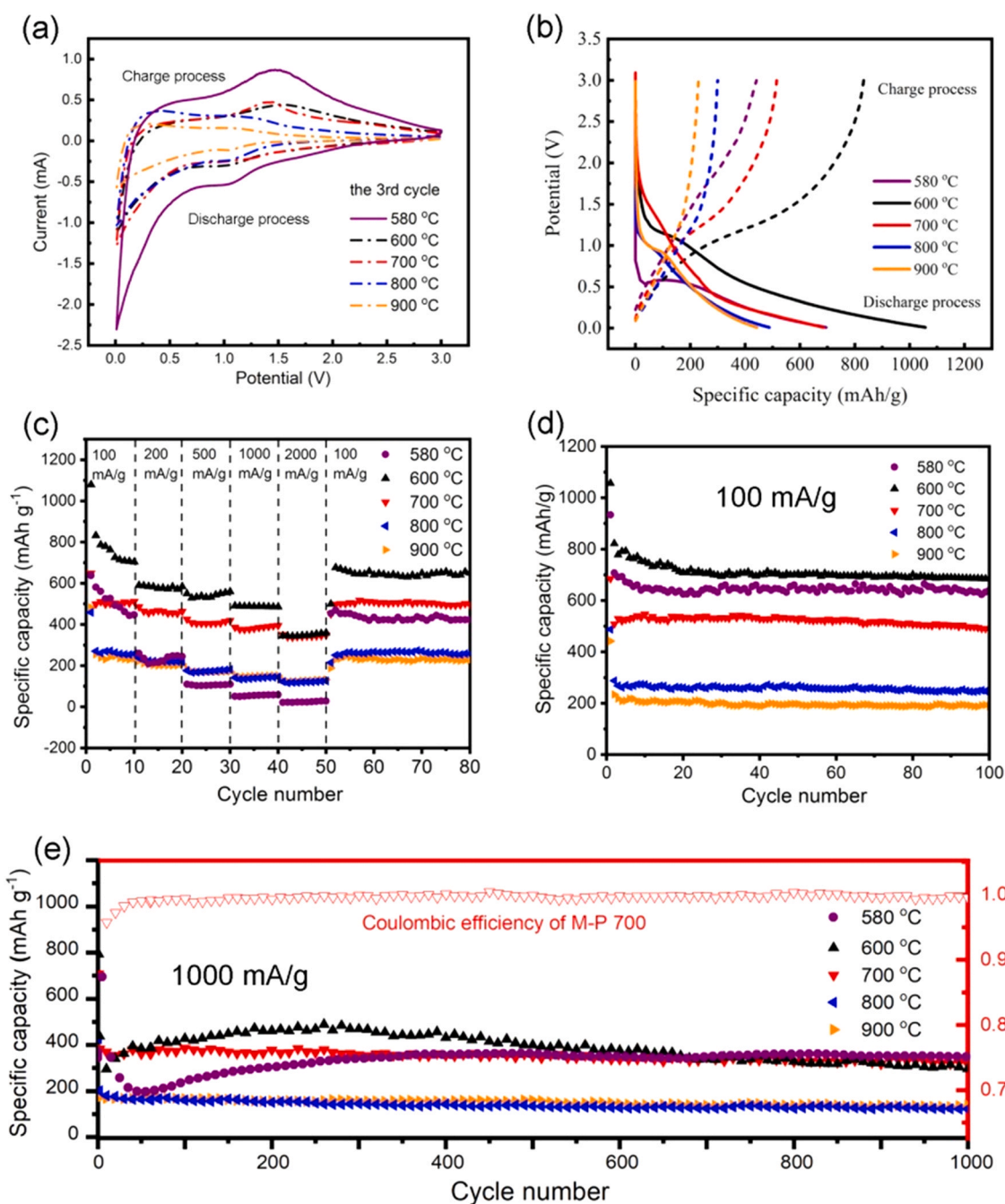


Fig. 7. Electrochemical performance of four electrodes made of M-P 580, M-P 600, M-P 700, M-P 800 and M-P 900. (a) The third-cycle CV profiles; (b) Voltage versus capacity curves at a current density of 100 mA g⁻¹ in the potential range of 0.01–3.00 V; (c) Rate performance of cells at different current densities; Cycling performance of cells at 100 mA g⁻¹ (d) and 1000 mA g⁻¹ (e), respectively.

electrode made of the M-P 580 exhibited an average discharge capacity of 518 mAh g⁻¹ at a low current density of 100 mA g⁻¹, and it restored to 427 mAh g⁻¹ when the current density bounced to 100 mA g⁻¹ after 50 cycles at different current densities. However, the capacity remained only 27 mAh g⁻¹ at a high current density of 2000 mA g⁻¹ due to the low crystallinity. The specific capacity of the M-P 600 was the highest in a current density range of 100–1000 mA g⁻¹, which was attributed to the dominant MoO₂ in the electrode, possessing a high theoretical specific capacity of 837 mAh g⁻¹, and the Mo₂N in the electrode, enhancing the conductivity of the electrode. The average discharge capacity of M-P 600 was 747 mAh g⁻¹ at a current density of 100 mA g⁻¹, which still maintained 349 mAh g⁻¹ at 2000 mA g⁻¹. When the current density was restored to

100 mA g⁻¹, the capacity reached 650 mAh g⁻¹, the highest value among the five samples. The electrode made of M-P 700 exhibited an average discharge capacity of 504 mAh g⁻¹ at a low current density of 100 mA g⁻¹, and it restored to 484 mAh g⁻¹ when the current density rebounded to 100 mA g⁻¹. The capacity remained 344 mAh g⁻¹ at a high current density of 2000 mA g⁻¹.

Compared to the M-P 580 and M-P 600 electrodes, the M-P 700 electrode displayed a more stable rate capability with slighter capacity decay between various current densities. For the M-P 800 and M-P 900 electrodes, the discharge capacities were 262 and 237 mAh g⁻¹ at a current density of 100 mA g⁻¹, respectively, and they retained 128 and 121 mAh g⁻¹ when the current density increased to 2000 mA g⁻¹. When the current density was recovered to 100 mA g⁻¹,

Table 1

Comparison of specific capacities of the Mo-based compounds/carbon electrodes prepared by electrospinning.

Materials	Current density (mA g ⁻¹)	Cycle number	Specific capacity (mAh g ⁻¹)	Refs.
MoO ₃ /coal-based CNFs	500	200	801.1	[28]
MoO _{2.8} /CNFs	200	250	876.9	[29]
MoO ₂ /CNFs	100	100	811	[30]
MoO ₂ @C nanofibers	500	600	665	[31]
MoO ₂ /Mo ₂ C/CNFs	100	70	1103.6	[18]
Mo ₂ C/N-doped CNFs	100	50	658	[32]
MoO ₂ /CNFs	100	100	636	This work
MoO ₂ /Mo ₂ N/CNFs	100	100	685	This work
Mo ₂ N/Mo ₂ C/CNFs	100	100	491	This work
Mo ₂ C/CNFs	100	100	189	This work

the two electrodes still exhibited reversible capacity values of 257 and 225 mAh g⁻¹, respectively, indicating that they also possessed stable rate performances. From above, it could be seen that the different electrodes showed a drastic change in the charge/discharge capacities, which resulted from the crystallinity and the content of different phase nanocrystals. When the annealing temperature was lower, the crystallinity of the anode materials was lower and their conductivity was worse. With the temperature increasing, the content of MoO₂ in the anode materials decreased, and the contents of Mo₂N and Mo₂C increased. Since the theoretical capacity of MoO₂ (837 mAh g⁻¹) [52] was larger than that of Mo₂C (524 mAh g⁻¹) [33] and Mo₂N (390 mAh g⁻¹) [53], thus, the capacity of the M-P 700–900 electrode was lower than that of the M-P 600 electrode.

Fig. 7d presented the cycling performance of five electrodes made of the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900, respectively. The results showed that the discharge capacities of M-P 580, M-P 600, M-P 700, M-P 800 and M-P 900 were 636, 685, 491, 247, and 189 mAh g⁻¹ after 100 cycles at a current density of 100 mA g⁻¹, respectively (Table 1). The capacities of M-P 580, M-P 600, M-P 700 and M-P 800 were higher than that of commercial carbon (372 mAh g⁻¹). In addition, all the five electrodes exhibited excellent cycling stability due to the structure of molybdenum-based compound nanoparticles/amorphous carbon nanofibers, in which the carbon nanofiber backbone played an important role in maintaining structural integrity during cycling [54].

To further evaluate the cycling performance of the electrodes at a high current density, we carried out endurance tests of five electrodes at 1000 mA g⁻¹. As illustrated in Fig. 7e, the five electrodes all exhibited excellent cycling stability. For the M-P 580 and M-P 600 electrodes, after initial decrease, the specific capacity first increased up to 300 cycles and then decreased after 300 cycles, while for the electrodes of the M-P 700, M-P 800 and M-P 900, the specific capacity remained fairly stable. The increase of specific capacity for the M-P 580 and M-P 600 electrodes might be caused by the activation process of the electrode materials [47,55,56], which was a common phenomenon when metal oxides were used as electrode materials. After 300 cycles, the specific capacity gradually decreased, yet still maintaining 350 and 300 mAh g⁻¹ after 1000 cycles at 1000 mA g⁻¹, which was 50.3% and 68.1% of the capacity value for the second cycle. The electrodes made of M-P 700, M-P 800 and M-P 900 showed excellent cycling stability, and their discharge capacity retained values of 318, 126 and 142 mAh g⁻¹ after 1000 cycles at 1000 mA g⁻¹ with a capacity retention of 82.5%, 61.7% and 80.1%, respectively (Table 2).

Compared with the electrode materials before cycling, the morphologies of the five electrodes materials exhibited no obvious changes after 1000 cycles at 1000 mA g⁻¹ (Fig. S20), demonstrating that the five electrodes had good stability. The excellent cycling stability of the five electrodes was mainly attributed to the composite of Mo-based nanocrystals encapsulated in the amorphous CNFs. The small nanocrystals in CNFs could provide additional electroactive sites. The amorphous carbon nanofibers could buffer the

Table 2Capacity retention of five electrodes made of the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900 at a current density of 1000 mA g⁻¹.

Electrodes	Capacity of second cycle (mAh g ⁻¹)	Capacity after 1000 cycles (mAh g ⁻¹)	Capacity retention (%)
M-P 580	695.6	350.0	50.3
M-P 600	440.4	300.1	68.1
M-P 700	385.8	318.4	82.5
M-P 800	204.4	126.1	61.7
M-P 900	177.5	142.2	80.1

drastic volume change of Mo-based nanocrystals during the insertion and extraction process of Li⁺ ions and also acted as a conducting framework for efficient electron transport. In addition, the carbon layer could effectively suppress the aggregation and dissolution of Mo-based compounds during the Li⁺ storage process. Thus, the Mo-based compounds nanocrystals/CNFs exhibited long cycling stability and excellent rate performance.

To further investigate the charge transport kinetics of the LIBs, EIS spectra were collected before cycling. Fig. 8a showed the Nyquist plots of M-P 580, M-P 600, M-P 700, M-P 800 and M-P 900 electrodes. The EIS spectra consisted of a semicircle in the high frequency region and an inclined line in the low frequency region. Fig. 8b exhibited the equivalent circuit model of the EIS spectra. R_s, R_{SEI} and R_{ct} represented the electrolyte resistance, transfer resistance of Li⁺ through the SEI film and transfer resistance of Li⁺ through the interface between electrolyte and electrode, CPE represented the double-layer capacitance and W represented the Warburg impedance associated with lithium diffusion. From Fig. 8a, it could be found that in the high frequency region, the semicircle diameter of the M-P 580 electrode was larger than those of the other four electrodes. This was mainly attributed to the poor conductivity caused by some partially-amorphous MoO₂ nanoparticles embedded in the amorphous carbon nanofibers in the M-P 580 electrode, as shown in Fig. 3(b). The semicircle diameters of the M-P 580, M-P 600, M-P 700, M-P 800, and M-P 900 gradually decreased, indicating that their contact and charge transfer impedance reduced with the annealing temperature increasing. This was attributed to the presence of Mo₂C and Mo₂N in the electrode produced at higher annealing temperatures which could increase the electric conductivity of the electrodes. The higher electric conductivity indicated that the rate performance was better for the electrode materials annealed at higher temperature. In addition, when increasing the annealing temperature from 580 to 900 °C, the diameter of the nanofibers gradually decreased from ~200 to ~150 nm, which shortened the diffusion length of Li⁺ ions and thus the slopes of the inclined lines in the low frequency region increased with the annealing temperature increasing. The slope of the M-P 600–900 electrode was larger than that of the M-P 580 electrode, indicating that Li⁺-ion diffusion was facilitated for electrode materials annealed at higher temperatures, which could enhance the long-term cycling stability. The EIS results showed that the higher the annealing temperature, the lower the

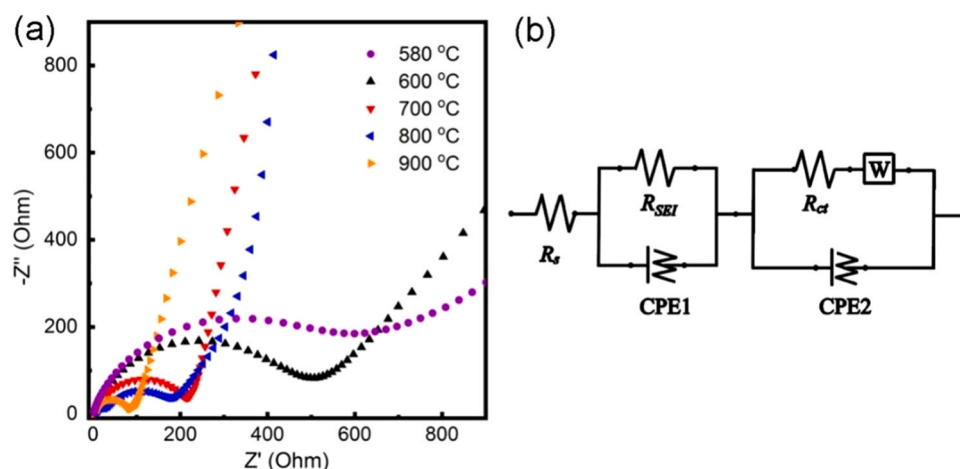


Fig. 8. EIS spectra and equivalent: (a) EIS spectra of M-P 580, M-P 600, M-P 700, M-P 800 and M-P 900 electrodes. (b) Equivalent circuit model of the EIS spectra.

contact and charge transfer impedance of the as-prepared electrodes, indicating that electrodes obtained at higher annealing temperatures could facilitate Li^+ ions transport into the electrode surface, and enhance the long-term recycling stability and rate performance.

4. Conclusions

In summary, a series of flexible CNF-based nanocomposite membranes embedded with various different types of Mo-based compound nanocrystals were fabricated with electrospinning technique and subsequent thermal annealing process. The Mo-based compound nanocrystals in the CNFs evolved from $\text{MoO}_2(\text{acac})_2$ to MoO_2 , Mo_2N and Mo_2C with the temperature increasing. In the Ar atmosphere, only $\text{MoO}_2(\text{acac})_2$ complexation and decomposition processes occurred in the nanofibers when the annealing temperature was lower than 500°C , and no crystalline structure was formed. A single-phase of MoO_2 was generated when the temperature increased to 580°C . With the temperature increasing, Mo_2N started to form with the reaction of MoO_2 and N atoms in the CNFs, and further converted into Mo_2C . When the temperature increased to 900°C , all the Mo_2N nanocrystals were transformed into Mo_2C , and a single-phase of Mo_2C was generated. All the LIBs employing Mo-based nanocrystals/CNFs as anodes exhibited excellent recycling stability, due to the buffer effect of the amorphous CNFs during the lithiation/de-lithiation process. The Mo-based nanocrystals/CNFs anodes that annealed at 600°C showed the highest specific capacity. Our work provides a facile and broadly-applicable strategy for the exact synthesis of Mo compound-based CNF composite materials with adjustable performances. The method for preparing various Mo-based compounds *via* tailoring the phase state of Mo compounds can be widely extended to the fabrication of other metal-based compounds for LIBs and other electrochemical devices.

CRediT authorship contribution statement

Tao Li: Methodology, Investigation, Writing-original draft. **Shouwu Gao:** Methodology, Investigation. **Kun Li:** Investigation. **Guiju Liu:** Investigation. **Xiaoli Sheng:** Investigation. **Dawei Shang:** Investigation. **Limin Wu:** Investigation. **Shaojuan Chen:** Methodology, Writing-review & editing. **Yiqian Wang:** Conceptualization, Methodology, Writing-review & editing, Supervision. **Shaohua Wu:** Methodology, Investigation, Writing-original draft, Writing-review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge financial support from High-end Foreign Experts Recruitment Programs (Grant Nos.: GDW20173500154, GDW20163500110), Shandong Province “Double-Hundred Talent Plan” (Grant No.: WST2018006), and the Top-notch Innovative Talent Program of Qingdao City, China (Grant no.: 13-CX-8). Y. Q. Wang also acknowledges financial support from the Taishan Scholar Program of Shandong Province, China, Qingdao International Center of Semiconductor Photoelectric Nanomaterials, and Shandong Provincial University Key Laboratory of Optoelectrical Material Physics and Devices.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jallcom.2022.168042](https://doi.org/10.1016/j.jallcom.2022.168042).

References

- [1] D. Zhao, J. Qin, L. Zheng, M. Cao, Amorphous vanadium oxide/molybdenum oxide hybrid with three-dimensional ordered hierarchically porous structure as a high-performance Li-ion battery anode, *Chem. Mater.* 28 (2016) 4180–4190, <https://doi.org/10.1021/acs.chemmater.6b00414>
- [2] B. Wang, X. Lu, Y. Tang, Synthesis of snowflake-shaped Co_3O_4 with a high aspect ratio as a high capacity anode material for lithium ion batteries, *J. Mater. Chem. A* 3 (2015) 9689–9699, <https://doi.org/10.1039/C5TA00140D>
- [3] Y. Liu, S.C. Wang, X. Sun, J.Y. Zhang, F.U. Zaman, L.R. Hou, C.Z. Yuan, Sub-nanoscale engineering of MoO_2 clusters for enhanced sodium storage, *Energy Environ. Mater.* 0 (2021) 1–9, <https://doi.org/10.1002/eeem2.12263>
- [4] G.Y. Wang, S.C. Wang, X. Sun, Y. Liu, P. Nie, L.R. Hou, L.M. Chang, C.Z. Yuan, Metallic Mo_2C quantum dots confined in functional carbon nanofiber films toward efficient sodium storage: heterogeneous interface engineering and charge-storage mechanism, *ACS Appl. Energy Mater.* 5 (2022) 1114–1125, <https://doi.org/10.1021/acsaem.1c03477>
- [5] C.J. Zhang, Y.P. He, Y.Q. Wang, Y.Z. Liang, A. Majeed, Z.L. Yang, S.S. Yao, X.Q. Shen, T.B. Li, S.B. Qin, CoFe_2O_4 nanoparticles loaded n-doped carbon nanofibers networks as electrocatalyst for enhancing redox kinetics in Li-S batteries, *Appl. Surf. Sci.* 560 (2021) 1449908, <https://doi.org/10.1016/j.apsusc.2021.1449908>
- [6] A.K. Haridas, J. Heo, X. Li, H. Ahn, X. Zhao, Z. Deng, M. Agostini, A. Matic, J. Ahn, A flexible and free-standing FeS/sulfurized polyacrylonitrile hybrid anode material

- for high-rate sodium-ion storage, *Chem. Eng. J.* 385 (2020) 123453, <https://doi.org/10.1016/j.cej.2019.123453>
- [7] S.S. Yao, C.J. Zhang, F.W. Xie, S.K. Xue, K.D. Gao, R.D. Guo, X.Q. Shen, T.B. Li, S.B. Qin, Hybrid membrane with SnS₂ nanoparticles decorated nitrogen-doped carbon nanofibers as binder-free electrodes with ultrahigh sulfur loading for lithium sulfur batteries, *ACS Sustain. Chem. Eng.* 8 (2020) 2707–2715, <https://doi.org/10.1021/acssuschemeng.9b06064>
 - [8] S.S. Yao, M.Z. Bi, H.L. Yu, C.J. Zhang, X.N. Zhang, H.T. Liu, T.J. Zhang, J. Xiang, X.Q. Shen, Spinel manganese-cobalt oxide nanospheres anchored on nitrogen-containing carbon nanofibers as a highly efficient redox electrocatalyst in lithium/polysulfides batteries, *Appl. Surf. Sci.* 598 (2022) 153787, <https://doi.org/10.1016/j.apsusc.2022.153787>
 - [9] S.S. Yao, Y.P. He, Y.Q. Wang, M.Z. Bi, Y.Z. Liang, A. Majeed, Z.L. Yang, X.Q. Shen, Porous n-doped carbon nanofibers assembled with nickel ferrite nanoparticles as efficient chemical anchors and polysulfide conversion catalyst for lithium-sulfur batteries, *J. Colloid Interface Sci.* 601 (2021) 209–219, <https://doi.org/10.1016/j.jcis.2021.05.125>
 - [10] S.C. Wang, Y. Liu, J.Y. Zhang, Y.Y. Wang, L.R. Hou, C.Z. Yuan, Flexible MoO₂ nanocrystals@N-doped carbon nanofibers film as a self-supporting anode for quasi-solid-state sodium-ion batteries, *Energy Technol.* 9 (2021) 2000820, <https://doi.org/10.1002/ente.202000820>
 - [11] J. Zhou, X. Li, C. Yang, Y. Li, K. Guo, J. Cheng, D. Yuan, C. Song, J. Lu, B. Wang, A quasi-solid-state flexible fiber-shaped Li-CO₂ battery with low overpotential and high energy efficiency, *Adv. Mater.* 31 (2019) 1804439, <https://doi.org/10.1002/adma.201804439>
 - [12] W. Devina, J. Hwang, J. Kim, Synthesis of MoO₂/Mo₂C/RGO composite in supercritical fluid and its enhanced cycling stability in Li-ion batteries, *Chem. Eng. J.* 345 (2018) 1–12, <https://doi.org/10.1016/j.cej.2018.03.130>
 - [13] S.H. Wu, T. Dong, Y.R. Li, M.C. Sun, Y. Qi, J. Liu, M.A. Kuss, S.J. Chen, B. Duan, State-of-the-art review of advanced electrospun nanofiber yarn-based textiles for biomedical applications, *Appl. Mater. Today* 27 (2022) 101473, <https://doi.org/10.1016/j.apmt.2022.101473>
 - [14] T. Li, D.W. Shang, S. W. Gao, B. Wang, H. Kong, G. Yang, W. Shu, P.L. Xu, G. Wei, Two-dimensional material-based electrochemical sensors/biosensors for food safety and biomolecular detection, *Biosensors* 12 (2022) 314, <https://doi.org/10.3390/bios12050314>
 - [15] B. Yu, D. Yang, Y. Hu, J. He, Y. Chen, W. He, Mo₂C nanodots anchored on n-doped porous CNT microspheres as electrode for efficient Li-ion storage, *Small Methods* 3 (2019) 1800287, <https://doi.org/10.1002/smt.201800287>
 - [16] X. Fan, X. Wang, G. Li, A. Yu, Z. Chen, High-performance flexible electrode based on electrodeposition of polypyrrole/MnO₂ on carbon cloth for supercapacitors, *J. Power Sources* 326 (2016) 357–364, <https://doi.org/10.1016/j.jpowsour.2016.05.047>
 - [17] W. Cho, J. Song, J. Kim, G. Jeong, E. Lee, Y. Kim, Electrochemical characteristics of nano-sized MoO₂/C composite anode materials for lithium-ion batteries, *J. Appl. Electrochem* 42 (2012) 909–915, <https://doi.org/10.1007/s10800-012-0470-9>
 - [18] H. Li, H. Ye, Z. Xu, C. Wang, J. Yin, H. Zhu, Freestanding MoO₂/Mo₂C imbedded carbon fibers for Li-ion batteries, *Phys. Chem. Chem. Phys.* 19 (2017) 2908–2914, <https://doi.org/10.1039/C6CP07569J>
 - [19] S. Wu, W. Zhao, M. Sun, P. He, H. Lv, Q. Wang, S. Zhang, Q. Wu, P. Ling, S. Chen, J. Ma, Novel bi-layered dressing patches constructed with radially-oriented nanofibrous pattern and herbal compound-loaded hydrogel for accelerated diabetic wound healing, *Appl. Mater. Today* 28 (2022) 101542, <https://doi.org/10.1016/j.apmt.2022.101542>
 - [20] Y. Li, T. Dong, Z. Li, S. Ni, F. Zhou, O.A. Alimi, S. Chen, B. Duan, M. Kuss, S. Wu, Review of advances in electrospinning-based strategies for spinal cord regeneration, *Mater. Today Chem.* 24 (2022) 100944, <https://doi.org/10.1016/j.mtchem.2022.100944>
 - [21] L. Ji, O. Toprakci, M. Alcoutlabi, Y. Yao, Y. Li, S. Zhang, B. Guo, Z. Lin, X. Zhang, A-Fe₂O₃ nanoparticle-loaded carbon nanofibers as stable and high-capacity anodes for rechargeable lithium-ion batteries, *ACS Appl. Mater. Interfaces* 4 (2012) 2672–2679, <https://doi.org/10.1021/am300333s>
 - [22] B. Li, X. Ge, F.W.T. Goh, T.S.A. Hor, D. Geng, G. Du, Z. Liu, J. Zhang, X. Liu, Y. Zong, Co₃O₄ nanoparticles decorated carbon nanofiber mat as binder-free air-cathode for high performance rechargeable zinc-air batteries, *Nanoscale* 7 (2015) 1830–1838, <https://doi.org/10.1039/C4NR05988C>
 - [23] G. Nie, X. Zhao, J. Jiang, Y. Luan, J. Shi, J. Liu, Z. Kou, J. Wang, Y. Long, Flexible supercapacitor of high areal performance with vanadium/cobalt oxides on carbon nanofibers as a binder-free membrane electrode, *Chem. Eng. J.* 402 (2020) 126294, <https://doi.org/10.1016/j.cej.2020.126294>
 - [24] L. David, R. Bhandavat, G. Singh, MoSS/graphene composite paper for sodium-ion battery electrodes, *ACS Nano* 8 (2014) 1759–1770, <https://doi.org/10.1021/nn406156b>
 - [25] S. Manzeli, D. Ovchinnikov, D. Pasquier, O.V. Yazyev, A. Kis, 2D transition metal dichalcogenides, *Nat. Rev. Mater.* 2 (2017) 17033, <https://doi.org/10.1038/natrevmater.2017.33>
 - [26] K. Kang, S. Xie, L. Huang, Y. Han, P. Huang, K.F. Mak, C.J. Kim, D. Muller, J. Park, High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity, *Nature* 520 (2015) 656–660, <https://doi.org/10.1038/nature14417>
 - [27] X. Cao, B. Zheng, W. Shi, J. Yang, Z. Fan, Z. Luo, X. Rui, B. Chen, Q. Yan, H. Zhang, Reduced graphene oxide-wrapped MoO₃ composites prepared by using metal-organic framework as precursor for all-solid-state flexible supercapacitors, *Adv. Mater.* 27 (2015) 4695–4701, <https://doi.org/10.1002/adma.201501310>
 - [28] X. Zhao, W. Jia, X. Wu, Y. Lv, J. Qiu, J. Guo, X. Wang, D. Jia, J. Yan, D. Wu, Ultrafine MoO₃ anchored in coal-based carbon nanofibers as anode for advanced lithium-ion batteries, *Carbon* 156 (2020) 445–452, <https://doi.org/10.1016/j.carbon.2019.09.065>
 - [29] X. Liu, H. Xu, Y. Huang, X. Hu, Direct planting of ultrafine MoO₂/s nanofibers in carbon nanofibers by electrospinning: self-supported mats as binder-free and long-life anodes for lithium-ion batteries, *Phys. Chem. Chem. Phys.* 18 (2016) 19832–19837, <https://doi.org/10.1039/C6CP01806H>
 - [30] J. Xiang, Z. Wu, X. Zhang, S. Yao, Enhanced electrochemical performance of an electrospun carbon/MoO₂ composite nanofiber membrane as self-standing anodes for lithium-ion batteries, *Mater. Res. Bull.* 100 (2018) 254–258, <https://doi.org/10.1016/j.materresbull.2017.12.045>
 - [31] Z. Chen, T. Yang, H. Shi, T. Wang, M. Zhang, G. Cao, Single nozzle electrospinning synthesized MoO₂@C core shell nanofibers with high capacity and long-term stability for lithium-ion storage, *Adv. Mater. Interfaces* 4 (2017) 1600816, <https://doi.org/10.1002/admi.201600816>
 - [32] R. Li, S. Wang, W. Wang, M. Cao, Ultrafine MoO₂ nanoparticles encapsulated in n-doped carbon nanofibers with enhanced lithium storage performance, *Phys. Chem. Chem. Phys.* 17 (2015) 24803–24809, <https://doi.org/10.1039/C5CP03890A>
 - [33] Y. Zhu, X. Ji, L. Yang, J. Jia, S. Cheng, H. Chen, Z. Wu, D. Passarello, M. Liu, Targeted synthesis and reaction mechanism discussion of Mo₂C based insertion-type electrodes for advanced pseudocapacitors, *J. Mater. Chem. A* 8 (2020) 7819–7827, <https://doi.org/10.1039/D0TA00697A>
 - [34] Y. Zhu, S. Wang, Y. Zhong, R. Cai, L. Li, Z. Shao, Facile synthesis of a MoO₂-Mo₂C-C composite and its application as favorable anode material for lithium-ion batteries, *J. Power Sources* 307 (2016) 552–560, <https://doi.org/10.1016/j.jpowsour.2016.01.014>
 - [35] C. Kim, S. Park, J. Cho, D. Lee, T. Park, W. Lee, K. Yang, Raman spectroscopic evaluation of polyacrylonitrile-based carbon nanofibers prepared by electrospinning, *J. Raman Spectrosc.* 35 (2004) 928–933, <https://doi.org/10.1002/jrs.1233>
 - [36] M.S.A. Rahaman, A.F. Ismail, A. Mustafa, A review of heat treatment on polyacrylonitrile fiber, *Polym. Degrad. Stabil.* 92 (2007) 1421–1432, <https://doi.org/10.1016/j.polyimdegstab.2007.03.023>
 - [37] B.G. Min, T.V. Sreekumar, T. Uchida, S. Kumar, Oxidative stabilization of PAN/SWNT composite fiber, *Carbon* 43 (2005) 599–604, <https://doi.org/10.1016/j.carbon.2004.10.034>
 - [38] K. Hamid, N.J. Reza, N. Srinivas, G. Gelayol, B. Khashayar, M.F. Seyed, K. Satish, N. Minoo, PAN precursor fabrication, applications and thermal stabilization process in carbon fiber production: experimental and mathematical modelling, *Prog. Mater. Sci.* 107 (2020) 100575, <https://doi.org/10.1016/j.pmatsci.2019.100575>
 - [39] R.K. Thomas, J. Penfold, Thermodynamics of the air–water interface of mixtures of surfactants with polyelectrolytes, oligoelectrolytes, and multivalent metal electrolytes, *J. Phys. Chem. B* 122 (2018) 12411–12427, <https://doi.org/10.1021/acs.jpcc.8b10350>
 - [40] Z. Yang, Z. Chang, Q. Zhang, K. Huang, X. Zhang, Decorating carbon nanofibers with Mo₂C nanoparticles towards hierarchically porous and highly catalytic cathode for high-performance Li-O₂ batteries, *Sci. Bull.* 63 (2018) 433–440, <https://doi.org/10.1016/j.scib.2018.02.014>
 - [41] H. Yan, Y. Xie, Y. Jiao, A. Wu, C. Tian, X. Zhang, L. Wang, H. Fu, Holey reduced graphene oxide coupled with an Mo₂N-Mo₂C heterojunction for efficient hydrogen evolution, *Adv. Mater.* 30 (2018) 1704156, <https://doi.org/10.1002/adma.201704156>
 - [42] R.S. Wise, E.J. Markel, Synthesis of high surface area molybdenum nitride in mixtures of nitrogen and hydrogen, *J. Catal.* 145 (1994) 344–355, <https://doi.org/10.1006/jcat.1994.1043>
 - [43] W. Marchal, C.D. Dobbelaere, J. Kesters, G. Bonneux, J. Vandenberghe, H. Damm, T. Junkers, W. Maes, J. D'Haen, M.K.V. Baelac, A. Hardy, Combustion deposition of MoO₃ films: from fundamentals to OPV applications, *RSC Adv.* 5 (2015) 91349–91362, <https://doi.org/10.1039/C5RA18001e>
 - [44] S. Musić, A. Šarić, S. Popović, Formation of nanosize ZnO particles by thermal decomposition of zinc acetylacetonate monohydrate, *Ceram. Int.* 36 (2010) 1117–1123, <https://doi.org/10.1016/j.ceramint.2009.12.008>
 - [45] G. Jin, R. Zhao, Y. Luo, J. Gao, G. Sun, Molybdenum oxide in CH₄/H₂ study on the mechanism of reduction and carbonization in atmosphere, *J. Fuel Chem. Technol.* 36 (2008) 738–742 (<http://www.cqvip.com/qk/90650x/200806/29031995.html>).
 - [46] T. Mo, J. Xu, Y. Yang, Y. Li, Effect of carburization protocols on molybdenum carbide synthesis and study on its performance in CO hydrogenation, *Catal. Today* 261 (2016) 101–115, <https://doi.org/10.1016/j.cattod.2015.07.014>
 - [47] Y. Shi, B. Guo, S.A. Corr, Q. Shi, Y. Hu, K.R. Heier, L. Chen, R. Seshadri, G.D. Stucky, Ordered mesoporous metallic MoO₂ materials with highly reversible lithium storage capacity, *Nano Lett.* 9 (2009) 4215–4220, <https://doi.org/10.1021/nl902423a>
 - [48] B. Guo, X. Fang, B. Li, Y. Shi, C. Ouyang, Y. Hu, Z. Wang, G.D. Stucky, L. Chen, Synthesis and lithium storage mechanism of ultrafine MoO₂ nanorods, *Chem. Mater.* 24 (2012) 457–463, <https://doi.org/10.1021/cm202459r>
 - [49] Q. Gao, L. Yang, X. Lu, J. Mao, Y. Zhang, Y. Wu, Y. Tang, Synthesis, characterization and lithium-storage performance of MoO₂/carbon hybrid nanowires, *J. Mater. Chem.* 20 (2010) 2807–2812, <https://doi.org/10.1039/B921001F>
 - [50] J. Liu, S. Tang, Y. Lu, G. Cai, S. Liang, W. Wang, X. Chen, Synthesis of Mo₂N nanolayer coated MoO₂ hollow nanostructures as high-performance anode materials for lithium-ion batteries, *Energy Environ. Sci.* 6 (2013) 2691–2697, <https://doi.org/10.1039/C3EE41006D>

- [51] Q. Gao, X. Zhao, Y. Xiao, D. Zhao, M. Cao, A. Mild, Route to mesoporous Mo₂C-C hybrid nanospheres for high performance lithium-ion batteries, *Nanoscale* 6 (2014) 6151–6157, <https://doi.org/10.1039/C3NR06678A>
- [52] Y. Yao, Z. Chen, R. Yu, Q. Chen, J. Zhu, X. Hong, L. Zhou, J. Wu, L. Mai, Confining ultrafine MoO₂ in a carbon matrix enables hybrid Li ion and Li metal storage, *ACS Appl. Mater. Interfaces* 12 (2020) 40648–40654, <https://doi.org/10.1021/acsaami.0c10833>
- [53] H. Yi, Y. Huang, Z. Sha, X. Zhu, Q. Xia, H. Xia, Facile synthesis of Mo₂N quantum dots embedded n-doped carbon nanosheets composite as advanced anode materials for lithium-ion batteries, *Mater. Lett.* 276 (2020) 128205, <https://doi.org/10.1016/j.matlet.2020.128205>
- [54] X. Gao, J. Wang, D. Zhang, K. Adair, K. Feng, N. Sun, H. Zheng, H. Shao, J. Zhong, Y. Ma, X. Sun, X. Sun, Carbon coated bimetallic sulfide nanodots/carbon nanorod heterostructure enabling long-life lithium-ion batteries, *J. Mater. Chem. A* 5 (2017) 25625–25631, <https://doi.org/10.1039/C7TA06849B>
- [55] Q. Tang, Z. Shan, L. Wang, X. Qin, MoO₂-graphene nanocomposite as anode material for lithium-ion batteries, *Electrochim. Acta* 79 (2012) 148–153, <https://doi.org/10.1016/j.electacta.2012.06.093>
- [56] Y. Sun, X. Hu, J. Yu, Q. Li, W. Luo, L. Yuan, W. Zhang, Y. Huang, Morphosynthesis of a hierarchical MoO₂ nanoarchitecture as a binder-free anode for lithium-ion batteries, *Energy Environ. Sci.* 4 (2011) 2870–2877, <https://doi.org/10.1039/C1EE01189H>