Hybrid Fibers



Highly Surface-Wrinkled and N-Doped CNTs Anchored on Metal Wire: A Novel Fiber-Shaped Cathode toward High-Performance Flexible Li–CO₂ Batteries

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Li-CO₂ batteries are regarded as a promising candidate for the next-generation high-performance electrochemical energy storage system owing to their ultrahigh theoretical energy density and environmentally friendly CO₂ fixation ability. Until now, the majority of reported catalysts for Li-CO₂ batteries are in the powder state. Thus, the air electrodes are produced in 2D rigid bulk structure and their electrochemical properties are negatively influenced by binder. The nondeformable feature and unsatisfactory performance of the cathode have already become the main obstacles that hinder Li-CO₂ batteries toward ubiquity for wearable electronics. In this work, for the first time, a flexible hybrid fiber is reported comprising highly surface-wrinkled and N-doped carbon nanotube (CNT) networks anchored on metal wire as the cathode integrated with high performance and high flexibility for fibershaped Li-CO₂ battery. It exhibits a large discharge capacity as high as 9292.3 mAh g⁻¹, an improved cycling performance of 45 cycles, and a decent rate capability. A quasi-solid-state flexible fiber-shaped Li-CO₂ battery is constructed to illustrate the advantages on mechanical flexibility of this fibershaped cathode. Experiments and theoretical simulations prove that those doped pyridinic nitrogen atoms play a critical role in facilitating the kinetics of CO₂ reduction and evolution reaction, thereby enabling distinctly enhanced electrochemical performance.

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1. Introduction

Since lithium-ion batteries (LIBs) were invented in 1990s, portable electronics industry has been keeping a fast pace of revolution and provided tremendous convenience for human's daily life.^[1-4] However, commercial LIBs based on LiCoO₂/graphite system which are produced in 2D rigid bulk structure gradually cannot satisfy the rapidly developing requirements on flexibility and energy storage of power accessory, as wearable consumer electronics appear.^[5-10] It is necessary to exploit alternative high-performance flexible energy storage devices to break through the inherent obstacles of current LIBs.^[11–17]

Metal–gas batteries have attracted numerous interests in recent years, due to their much higher theoretical energy density than that of commercial LIBs (\approx 350 Wh kg⁻¹ for LIBs, 3500 Wh kg⁻¹ for Li–O₂ batteries).^[15–19] Among them, a new family of Li–CO₂ batteries was proposed as a promising candidate for the next-

generation high-performance energy storage systems, because of their superior lithium storage and environmentally friendly CO_2 fixation capability.^[20–25] At present, a few species have proved to be effective in Li–CO₂ batteries, including carbon materials,^[20,21,24,25,27,32,33] rare metal Ru\Ir,^[26,28,34–36] transition metal Cu\Mo\Ni,^[37–39] and their derivatives.^[29–31,40] Among them, carbon nanophases, like super P,^[20,22,24] carbon nanotube (CNT),^[21,32,33] and graphene,^[25,27] are mainly utilized as the active solid catalysts owing to their relatively stable structure, light weight, and low expenditure when compared with those metal-based catalysts.^[28,34,35,38]

Despite several microstructure modifications have been implemented to optimize the electrochemical performances of carbon-based catalysts,^[27,37,40] flexible Li–CO₂ battery devices were less frequently reported until now,^[33] expecially for 1D fiber-shaped batteries which exhibit superior geometrical conformability to irregular surface than their planar counterparts, enabling them more attractive to wearable electronics.^[6,10,14,17,41] The difficulty on fabricating 1D flexible Li–CO₂ batteries mainly lies in how to design and synthesize fiber-shaped flexible



cathodes with efficient catalytic activity and enough mechanical strength. First of all, for conventional catalysts in powder state which dominate Li-CO₂ batteries, it was inevitable to be mixed with polymer binder and subsequently attached to 2D rigid current collectors (carbon paper and nickel foam), making the electrodes nondeformable.^[27,30,39] It is obvious that this coating strategy is not appropriate to fabricate fiber-shaped electrodes on account of geometric factors and these rigid electrodes are detrimental to achieve flexibility of energy storage devices.^[15,42] Meanwhile, traditional carbon nanophases only show a quite limited catalytic activity, and the introduction of polymer binder causes parasitic reactions together with conductivity decline of electrode, which results that current Li-CO₂ batteries usually suffer from an unsatisfying cycle stability and poor rate capability.^[20,21,25,33] Hence, the majority of previous Li-CO₂ batteries are hardly to take care of both electrochemical performance and mechanical flexibility at the same time.^[32,33,35] This dilemma has already dominated the challenges that are impending Li-CO₂ batteries toward practical application. Second, affected by high aspect ratios, the transport path of electrons of 1D electrode has been drastically extended by order of magnitudes and the spontaneous agglomeration of materials is more likely to occur on hook face to minimize surface energy as well, directly inducing the distinct decay on electrochemical activity.^[43–45] As a consequence, the electrochemical performance of fiber-shaped energy devices is not comparable to that of planar devices, frequently.^[16,44,46,47] In this regard, developing 1D highly conductive flexible electrodes with more efficient catalyst networks homogenously distributed on surface underlies the construction of high-performance flexible fiber-shaped Li-CO₂ batteries for wearable electronics.^[8,44,48]

In this work, for the first time, we fabricated a novel binderfree and free-standing flexible fiber-shaped cathode for Li-CO₂ batteries, where highly surface-wrinkled and N-doped CNT networks are homogenously anchored on the surface of Ti wires (denoted as N-CNTs@Ti) via a floating catalytic chemical vapor deposition (FCCVD) strategy. On one hand, the introduction of metal wires not only ensures the high conductivity of electrode but also provides a highly flexible substrate with enough mechanical strength to achieve the deformable characteristic as well as the uniform in situ growth of N-CNTs. On the other hand, highly wrinkled surface and N-doping can bring in more defects and active sites into CNTs, thus significantly promoting the catalytic activity for both CO₂ reduction reaction (CO₂RR) and evolution reaction (CO2ER). Based on the aforementioned advantages, N-CNTs@Ti free-standing composite fibers exhibited more superior electrochemical performances than those of traditional 2D CNTs-based Li-CO2 battery cathodes, namely, it delivered a large discharge capacity of 9292.3 mAh g⁻¹, a good cycling stability for 45 cycles, and a decent rate capability. Given that high performance and high flexibility are synchronously integrated into N-CNTs@Ti, this fiber-shaped cathode was subsequently employed to assemble a quasi-solid-state flexible fiber-shaped Li-CO₂ battery, of which the function remained stable under various deformation conditions. Additionally, a series of characterizations coupled with density function theory (DFT) study revealed that Li₂CO₃ could be reversibly deposited and decomposed on the wrinkled walls of N-CNTs, and the doped pyridinic nitrogen atoms (N-6) should play a vital

role of bridge in facilitating the reaction kinetics of CO₂ER and CO₂RR by coordinative electron transfer, thus leading to much enhanced energy storage capability. Except for metal–gas batteries, it is believed that the specially designed N-CNTs@Ti flexible fiber can be also applied in other fields, such as super-capacitor, sensor, intelligent response, and biomedicine.

2. Results and Discussion

2.1. Physical Characterization

Figure 1 schematically elucidates the fabrication procedure of N-CNTs@Ti free-standing fiber-shaped electrode and the subsequent assembly of flexible fiber-shaped Li-CO₂ battery. Following the dissolution of imidazole $(C_3H_4N_2)$ and ferrocene $(Fe(C_5H_5)_2)$ in CH₃CN, the obtained red solution, which worked as carbon sources and catalysts, was transferred into a quartz boat placed in the front of a furnace tube. After that, the Ti wire with a certain length was deeply cleaned up and fixed in another quartz boat behind the above red solution. Next, the entire system was subjected to heat treatment (i.e., FCCVD process) for a short time at 850 °C with Ar as the carrier gas, allowing the in situ growth of highly N-doped CNT networks on the surface of Ti wire. When the furnace cooled down naturally, the flexible N-CNTs@Ti fiber was obtained without further purification. Finally, the as-prepared N-CNTs@Ti fiber was wrapped on the gel polymer electrolyte (GPE) coated lithium wire to assemble an all-solid-state flexible fiber-shaped Li-CO2 battery, as proof-of-concept application. Additionally, it should be pointed out that this synthesis approach seems to be a versatile method for preparing other flexible metal-CNTs fibers, such as Al-CNTs, Cu-CNTs, and Ni-CNTs fibers. The liquid-vapor-solid conversion strategy of catalysts enables it quite suitable for scalable and continuous industrial production as well.

From the X-ray diffraction (XRD) patterns presented in **Figure 2**a, all the sharp diffraction peaks are ascribed to metal Ti wire (JCPDS No. 44–1288), except for the obvious peak at ≈26.2°,



Figure 1. Schematic illustrating the synthesis procedure of N-CNTs@ Ti electrode and the inner configuration of as-fabricated flexible fibershaped device. a) Pristine Ti wire. b) Spring-like Ti wire obtained by wrapping the pristine one. c) In situ growth of N-CNT networks on Ti wire by floating catalytic chemical vapor deposition. d) The surface-wrinkled N-doped CNT networks anchored on the surface of Ti. e) Configuration of the as-fabricated quasi-solid-state flexible fiber-shaped Li–CO₂ battery employing N-CNTs@Ti as working electrode and its working principle.

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Figure 2. a) XRD patterns of the pristine Ti wire, pure CNT powders, and as-synthesized N-CNTs@Ti. Typical SEM images of N-CNTs@Ti at b) top view and c) cross-sectional view with the EDS element mappings of C and Ti inset. d) SEM, e) TEM, and f,g) HRTEM images of N-doped CNTs in situ growing on Ti wire. A SAED pattern is shown in inset in (f). h) STEM image and corresponding element mappings of C, N, and O of an individual N-doped CNT. i) Digital photographs depicting the high flexibility of N-CNTs@Ti fiber under different deformation conditions.

which belongs to the (002) planes of graphite carbon, implying the high crystallinity and high phase purity of N-CNTs as well as the successful hybridization of Ti and N-CNTs.^[46,49,50] The morphology of N-CNTs@Ti has been first examined by scanning electron microscope (SEM). As can be seen from Figure 2b and Figure S1a (Supporting Information), the Ti wire was covered by numerous fleece-like N-CNTs without recognizable agglomeration, making the electrode surface look much rougher than that of the pristine Ti wire (Figure S2, Supporting Information). The uniform distribution of N-CNTs has been proved by energy dispersive spectrum (EDS) element mappings in Figure 2c, where C element only appeared as a circle surrounding the outer edge of Ti element region. When examined the surface in detail, it was found that these N-CNTs with an average diameter of 150 nm entangled with each other forming a 3D highly interconnected porous network (Figure 2d; Figure S1b, Supporting Information). It is believed that the porous catalyst networks can provide more deposition space for discharge products of



Li-CO₂ batteries. Furthermore, transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were conducted to investigate the microstructure of N-CNTs grown on Ti wire. Unlike the smooth surface of ordinary CNTs (Figure S3, Supporting Information), the N-CNTs synthesized by FCCVD exhibited a remarkable distinction that they possessed a highly wrinkled nanotube walls (Figure 2e; Figure S1c-f, Supporting Information), of which the thickness was about 10 nm (Figure S1h, Supporting Information). Figure S1g (Supporting Information) further revealed the surface folding structure of N-CNTs. The inside selected area electron diffraction (SAED) pattern demonstrated the typical polycrystalline diffraction rings of CNT. These interlayers constituting wrinkles showed the distance of the adjacent lattice being 0.34 nm, in good accordance with standard (002) plane of graphite.^[12,51,52] Attractively, it can be also clearly discerned from Figure 2e that the N-CNT walls were so inconsecutive that plenty of voids (Figure 2f) and defects (Figure 2g; Figure S1i, Supporting Information) have been introduced into the surface, thus releasing more active atoms for CO₂RR and CO₂ER. Moreover, the scanning transmission electron microscope (STEM) image coupled with element mappings verified that those doped N atoms were highly dispersed in the whole CNT, as displayed in Figure 2h. The content of N atoms doped in the surface-wrinkled CNT was measured to be 3.68 wt%, which was proved by the results of energy dispersive X-ray (EDX) spectroscopy conducted on the selected area of N-CNT presented in Figure S4 (Supporting Information), indicating a relatively high N-doping level in carbon arrangement via this in situ growth strategy. According to the X-ray photoelectron spectroscopy (XPS) spectrum of N-CNTs@Ti and CNT powder shown in Figure S5a (Supporting Information), N 1s orbit can be only detected in our synthesized composite fiber and the content of doped N atoms was calculated to be 7.14 wt%. This value is higher than that of EDX measurement, of which the reason is considered to be the elimination of carbon signal interference caused by sample supporters like copper/carbon micromesh for TEM or the enrichment of N element on CNT surface, given that XPS is a surface sensitive characterization technology. Also, it can be recognized from the high-resolution XPS spectrum that pyridinic nitrogen (N-6, located at 398. 8 eV) and graphitic nitrogen (N-Q, located at 401. 0 eV) should be the main two categories of N-doping in the as-synthesized N-CNTs (Figure S5b, Supporting Information).^[27,53-55] Raman spectroscopy was implemented to further confirm the structure of N-doped CNT anchored on Ti and commercial CNT powder, with the results presented in Figure S6 (Supporting Information). It is obviously observed that the spectra reveal two main characteristic peaks located at 1340 and 1581 cm⁻¹ which correspond to D (sp^[3] hybridization and disordered carbon) and G (sp^[2] hybridization) bands of carbon materials, respectively. It is well-known that the intensity ratio of D and G bands (I_D/I_G) can mirror the crystallinity of graphite, which hence is commonly regarded as an important index to evaluate the quality of carbon nanophases.^[4,12,52] The I_D/I_G value of N-CNTs@Ti (1.05) is higher than that of CNT powder (0.98), demonstrating that there are more structural defects exposed in the N-doped hexagonal-close-packed carbon lattice of our synthesized sample. Besides, it is also noteworthy that N-CNTs@ Ti free-standing fibers demonstrated outstanding mechanical flexibility. It was easy for them to tolerate various kinds of

drastic deformations, like bending, knotting, and twisting (see Figure 2i), which solidified the foundation for the following fabrication of flexible fiber-shaped Li– CO_2 battery, as a result.

2.2. Electrochemical Studies

2.2.1. Electrochemical Behavior of N-CNTs@Ti

Considering that porous structure and high conductivity are two necessary features for metal-gas battery catalysts, N-CNTs@ Ti fibers were employed as the flexible cathodes for Li–CO₂ batteries. First, the electrochemical behaviors of N-CNTs@Ti have been studied using cyclic voltammetry (CV), with the results presented in Figure S7 (Supporting Information). It can be observed that only a reduction peak located at 2.40 V appears at the first cathodic scanning, which is ascribed to the interaction of Li and CO₂ forming Li₂CO₃ and C based on the formula: $4Li^+ + 3CO_2 + 4e^- \rightarrow 2Li_2Co_3 + C$. During the subsequent anodic sweep, the response current suddenly arose when the voltage reached at 4.18 V, indicating that the discharge product started to decompose and allowed the release of CO₂ at high voltage. The CV results of N-CNTs@Ti are well consistent with those of other CNT-based Li-CO2 batteries reported previously.^[25,30,34,39] Interestingly, to evidence the generation of carbon in discharge products of Li-CO2 batteries, surface enhanced Raman spectroscopy (SERS) was conducted on a Al mesh coated with Au nanoparticles (denoted as ALM@Au) as the none carboncontaining cathode for Li-CO₂ battery, considering the disturbance of C signals caused by CNT if common characterization methods were utilized, like XRD, EDS, or EDX. Obviously, there are no characteristic D and G bands regarding sp3 and sp2 hybridization of carbon that can be detected in the cathode before discharge. Whereas, the above two vibration peaks of carbon which are located at \approx 1350 and 1587 cm⁻¹ can be observed in the Raman spectrum after discharge (Figure S8, Supporting Information), giving a proof of the fact that carbon was really generated as one of the discharge products of Li-CO₂ battery. Moreover, the electrochemical performance has been further assessed by galvanostatic charge-discharge tests. As can be seen from Figure 3a, it reproduces the initial discharge profiles of N-CNTs@Ti and CNTs powders at a current density of 50 mA g⁻¹. The voltage of CNT powders decreases rapidly as discharge process proceeds and only 4461.2 mAh g⁻¹ is recorded when the voltage declines to 2.2 V. In comparison, N-CNTs@Ti shows a long and flat plateau at around 2.65 V, delivering a large capacity of 9292.3 mAh g⁻¹ under the same condition, which is nearly 2.1 times as much as that of CNT powders. It implies that more CO₂ catalytic sites and promoted reduction kinetics have been simultaneously imported into the cell with a N-CNTs@Ti cathode. To exclude potential catalytic effect contributed by Ti substrate, the electrochemical behaviors of the pristine Ti wire and the Ti wire after the same calcination process without carbon resources and catalyst precursors were studied, additionally. The extremely rapid voltage decline below 2.2 V happens in the case of pristine Ti wire, while the capacity of Ti wire after calcination is neither recognizable, as revealed in the discharge profiles of Figure S9 (Supporting Information). The negligible difference between these two Ti wire samples is

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Figure 3. a) Galvanostatic discharge/charge profiles of N-CNTs@Ti and CNT powder under CO_2 at a current density of 50 mA g⁻¹. Cycling performances of N-CNTs@Ti electrode for the selected cycles at the current density of b) 50 and c) 250 mA g⁻¹ with the controlled capacity of 1000 mAh g⁻¹. d) Rate capabilities of the Li–CO₂ cells with a N-CNTs@Ti cathode and a CNT powder cathode, respectively. e) Galvanostatic discharge/charge profiles of the N-CNTs@Ti cathode at different current densities. f) Polarizations of N-CNTs@Ti and CNT powder cathodes during the rate tests. The polarizations are calculated based on the charge and discharge voltage difference at various current densities.

mainly caused by the amorphous oxide layer on Ti wire after calcination. Based on the aforementioned results, it is believed that Ti wire makes no influence on CO₂ reduction process but acts as a flexible substrate to simultaneously provide rough surface for in situ growth of active surface-wrinkled N-doped CNT networks and ensure the high electroconductivity of the whole electrode. Besides, the N-CNTs@Ti electrode has an excellent cycling stability as well. It can be reversibly discharged and charged for 25 cycles at 50 mA g⁻¹ with the controlled capacity of 1000 mAh g⁻¹, and even normally work for over 700 h, as indicated in Figure 3b and Figure S10a (Supporting Information). The median voltages of discharge/charge plateaus have a little fluctuation at \approx 2.73 and \approx 4. 24 V, respectively, while the corresponding energy efficiencies are calculated to be ≈65% (Figure S10b, Supporting Information). When the applied current density is larger at 250 mA g⁻¹, N-CNTs@Ti can steadily last for 45 cycles, as proved by Figure 3c and Figure S11a (Supporting Information). It should be pointed out that the discharge voltage still maintains at nearly 2.5 V at the end of 45th cycle, which is comparable to that of the initial cycle, giving a proof of the fact that the catalytic activity of N-CNTs@Ti has been well reserved after the cycling process (Figure S11b, Supporting Information). These nearly constant discharge end voltages further suggest that N-CNTs@Ti can effectively prevent its active components from the structural damage caused by those superoxide radicals (such as O_{2}^{-}) that are generated through decomposing discharged products. For comparison, N-CNTs powder cathode can only deliver a limited cycling stability of less than 13 cycles at 250 mA g⁻¹ (Figure S12, Supporting Information), which is much inferior than that of N-CNTs@Ti fibershaped cathode. Simultaneously, the average discharge voltage of N-CNTs powder is distinctly lower when compared with that of N-CNTs@Ti electrode at the same current density. This result further verified the advantageous properties of N-CNTs@Ti fiber on maintaining catalytic activity against potential structural damage caused by producing or decomposing discharge



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products as well as promoting the CO2-related catalytic reaction kinetics. Nevertheless, it is noteworthy that, in contrast to 25 cycles at 50 mA g⁻¹, N-CNTs@Ti demonstrates more superior cycle longevity at the higher rate of 250 mA g⁻¹, in which less voltage fluctuation can be observed in the galvanostatic discharge/charge profiles. We consider that the instability of aprotic electrolyte for Li-CO₂ battery under high voltage (>4. 2 V) may partially explain the reason. To be specific, low current density means that the electrolyte has to tolerate structural damage longer at high voltage, leading to a higher risk of electrolyte decomposition during the charge process (e.g., 20 h for 50 mA g⁻¹ and 4 h for 250 mA g⁻¹ per cycle). In spite of 25 cycles, the working time of N-CNTs@Ti electrode reaches 770 h at 50 mA g^{-1} , which is remarkably larger than 350 h of the one cycling at 250 mA g⁻¹. This phenomenon has been also observed in some previous catalysts for Li-CO₂ batteries, like Ru@Super P28 and Ir NSs-CNFs, [56] where invalidation of electrolyte should be one of the dominant factors that give rise to the performance decay of the battery. The morphology differences of discharge products may be another factor to explain the distinct cycling stability at low and high current density. It can be observed from Figure S13 (Supporting Information) that the surface of N-CNTs was covered with a dense film-like products after discharging at 50 mA g⁻¹ while brush-like nanosheets were formed on N-CNTs in the case of discharging at 250 mA g⁻¹. The interconnected brush-like nanosheets with abundant gaps between each other are considered to be decomposed more easily compared with these dense film-like discharge products when discharging, on account of the faster gas diffusion. Another important electrochemical evaluation indicator, rate capability, was subsequently investigated by discharging and charging the Li-CO₂ cells for three times at every diverse current density with a curtailing capacity of 1000 mAh g⁻¹ (Figure 3d). As the current rate increases from 0. 05 to 0.1, 0.2, 0.5, and 1 A g⁻¹, the N-CNTs@Ti fiber displays flat discharge plateaus at 2.83, 2.70, 2.54, 2.41, and 2.30 V (Figure 3e), respectively, which are significantly higher than those of its 2D counterpart (Figure S14, Supporting Information). Meanwhile, the composite fiber also delivers lower charge potential during the rate tests, as observed in Figure S15 (Supporting Information). When the current density goes back to 0.05 A g^{-1} after being discharged/charged at high rates for 15 cycles, N-CNTs@Ti can regain an average discharge voltage of 2.78 V for another 3 cycles, without obvious voltage decay compared to 2.83 V obtained in the initial cycles at 50 mA g^{-1} , implying that the electrode structure integrity survived in the impact of high current. In addition, Figure 3f compares the polarizations of N-CNTs@Ti and CNT powder cathodes during the rate tests. The lower polarization of N-CNTs@Ti further implies that our synthesized composite fibers possess a significantly enhanced catalytic reaction kinetics. Excellent rate performance means that higher working voltage can be realized in the extreme environment requiring large current, which endows the batteries with an increased energy density, thereby enlarging the longevity of electric consumer equipment, especially those for space exploration.

After comparing with other typcial fiber-shaped energy storage devcies, it is found that this $Li-CO_2$ battery with a fiber-shaped N-CNTs@Ti electrode delivered a remarkably

higher discharge capacity of 9292.3 mAh g⁻¹ based on the weight of N-CNTs on cathode, which is about 67 times larger than that of the fiber-shaped LIB consisting of LiMn₂O₄ and Li4Ti5O12,[57] 87 times higher than that of the fiber-shaped LIB generated by LiMn₂O₄ and Si,^[58] 84 times that of a 1D Na-ion battery,^[59] 55 times that of a Zn-C battery,^[60] 8.8 times that of a Li–S battery,^[45] 9.9 times that of a Al–O₂ battery,^[17] 7.4 times that of a Zn-O2 battery,^[61] and 1.5 times that of a Li-O2 battery,^[62] but $\approx 3/4$ that of an ambient Li-air battery,^[15] respectively, as shown in Figure S16 and Table S1 (Supporting Information). In addition, if take the weight of Ti wire into account, the energy density of the whole N-CNTs@Ti cathode is estimated to be 99.2 Wh kg⁻¹, still much higher than those of the fiber-shaped LIB (27 Wh kg⁻¹),^[57] and oders of magnitude larger than that of fiber-shaped supercapacitors (0.63 Wh kg⁻¹),^[63] due to the combined features of large specific capacity and high discharge plateau possessed by Li-CO₂ batteries. The energy density can be further improved by optimizing the fabrication process, such as in situ growth of surface-wrinkled N-CNTs on other lighter metal wires or highly conductive carbon nanofiber, carbon nanotube, and graphene based fiber-shaped substrates. Furthermore, the electrochemical performances of this fiber-shaped Li-CO2 battery were systematically summarized and compared with previous reports about Li-CO₂ batteries.^[20,21,25,28,32-34,36-40,64,65] For convenience, the detailed comparison has been listed in Table S2 (Supporting Information). Obviously, it mainly focuses on developing new kind of species with catalytic activity at current research satge so that quite limited Li-CO₂ batteries demonstrate mechanical flexibility owing to the indeformability of cathodes using stiff current collecters, like carbon paper. The incorporation of highly flexible N-CNTs@Ti cathode into battery can effectively tackle the above issue. Besides the highest discharge capacity among CNT-based cathodes, the as-synthesized N-CNTs@Ti electrode also exhibits better cycling stability to a certain extent than traditional carbon nanophases used for Li-CO₂ battery catalysts, like super P,^[20] CNTs,^[21] and graphene^[25] (≈20 cycles). While it is compared with previous transition metal/carbon composite catalysts, the cycling behavior of this fiber-shaped electrode is still comparable to those of Co/Mo/Ni/Cu^[30,37,38,40,64,65] or Ir/RuO₂^[34,36] based planar cathodes (about 50 cycles), but a little inferior than that of Ru/Super P²⁸ hybrid catalysts (70 cycles). Several other properties including state of electrolyte and discharge/charge plateau were also summarized in this table to provide a comprehensive insight into these Li-CO₂ batteries.

2.2.2. The Quasi-Solid-State Flexible Fiber-Shaped Li-CO₂ Battery

To better illustrate the advantage of N-CNTs@Ti on constructing flexible energy storage devices, a quasi-solid-state flexible fibershaped Li–CO₂ battery was fabricated using this as-synthesized hybrid fiber. Because of the introduction of GPE,^[15,32] this quasisolid-state Li–CO₂ battery will not take the risk of the leakage of electrolyte, compared with their liquid counterparts, as shown in **Figure 4**a. It is worth noting that the length of the fiber-shaped battery can be easily controlled by tuning the length of N-CNTs@ Ti hybrid fiber and Li wire, due to their unique 1D structure which is quite convenient for the assembly. Furthermore, this



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Figure 4. a) The photograph depicting the as-fabricated quasi-solid-state flexible fiber-shaped Li–CO₂ battery. b) A red LED lit up by a 5 cm fiber-shaped flexible Li–CO₂ battery at different bending angles. c–e) A strain sensor based on CNT/PDMS hybrid film which was powered by a 10 cm curving Li–CO₂ battery attached on human hand. f) Current–time curve of the strain sensor during the bending cycles of the finger.

quasi-solid-state fiber-shaped Li-CO2 battery exhibited high flexibility as well. From Figure 4b and Figure S17 (Supporting Information), it can be observed that the red light emitting diode (LED) was always lit up by the as-fabricated fiber-shaped Li-CO₂ battery in the bending angle range of 0°-180°, without obvious luminance change during the deformation. Interestingly, we also employed another 10 cm fiber-shaped Li-CO₂ battery to provide electricity for a flexible strain sensor based on CNT/polydimethylsiloxane (PDMS) hybrid film. This quasisolid-state flexible fiber-shaped Li-CO2 battery can favorably fit into the irregular surface of human hand (Figure 4c). During the repeated curving of the finger (Figure 4d,e), the strain sensor made a response immediately, which was certificated by the current-time curve displayed in Figure 4f. As a result, the aforementioned presentations revealed a great potential of this quasi-solid-state flexible fiber-shaped Li-CO₂ battery toward practical applications, especially on wearable electronics.

2.3. In Situ/Ex Situ Studies of N-CNTs@Ti Electrodes in Li–CO₂ Cells

2.3.1. Experimental Results

A series of ex situ and in situ characterizations were conducted to understand what has happened in the Li–CO₂ cell during cycling, aimed at further excavating the reason why N-CNTs@ Ti cathode could exhibit such a decent electrochemical performance. As demonstrated in the in situ Raman spectra of **Figure 5**a, apart from two main peaks which are always detected at 1343 and 1603 cm⁻¹ (D band and G band of N-CNTs), a broad peak belonging to Li₂CO₃ gradually emerges at 1120 cm⁻¹ as the discharge process proceeds, while this characteristic vibration mode continuously decreases when the battery is recharged.^[26,27,33] The above experimental results output that Li₂CO₃ can be reversibly formed and decomposed on cathode







Figure 5. a) The in situ Raman spectra of N-CNTs@Ti electrode at 11 selected points during cycling with the galvanostatic discharge/charge profiles on the left. b) XRD patterns of the pristine, discharged, and recharged N-CNTs@Ti. Typical TEM images of N-CNTs extracted from N-CNTs@Ti after c) the first discharge process and d) the following charge process. The high-resolution XPS spectra of C 1s and N 1s orbits for N-CNTs@Ti at different states: e,h) pristine, f,i) discharged, and g,j) recharged.

under the assistance of N-CNTs catalyst during the discharge/ charge cycles, which hence achieves the rechargeability of this newly designed Li–CO₂ battery. The XRD results presented in Figure 5b further give an evidence of the reversible formation and decomposition of crystalline Li₂CO₃ during the roundtrip, as the diffraction peaks ascribed to Li₂CO₃ appear after discharging and disappear after charging. The reversible formation of Li₂CO₃ has also been certificated by SEM (Figure S18, Supporting Information) and TEM (Figure 5c,d). After being fully discharged at 100 mA g⁻¹, the surface of N-CNTs was covered by a certain kind of film-like agglomeration, as can be clearly observed in Figure 5c and Figure S18b (Supporting Information). By contrast, only bare nanotubes can be found in the cases of pristine N-CNTs (Figure S18a, Supporting Information) and recharged N-CNTs (Figure 5d; Figure S18c, Supporting Information). Furthermore, surface-sensitive XPS was performed to analyze the chemical state changes of N-CNTs@Ti. As can be seen in the C 1s and N 1s spectra of pristine N-CNTs@Ti, two binding energy peaks located at 286.4 and 284.8 eV should be assigned to C–O and C–C bonds (Figure 5e),^[38,40,66] while four various categories of doped N atoms (N-6, N-5, N-Q, and N-O) contribute to the peaks around 398.4, 399.5, 401.0, and 402.6 eV (Figure 5h).^[27] When discharge product is deposited, the intensity of the peak reflecting C–O bond is significantly augmented and another two new peaks occur at 292.9 and 290.0 eV, of which the former is originated from electrolyte and the latter is ascribed to Li₂CO₃ (Figure 5f).^[37,40] After the battery is completely recharged, the C–O peak returns to the initial figure and the peak associated with Li₂CO₃ totally disappears (Figure 5g), which demonstrates that the discharge product







Figure 6. Top view of the optimized energetically most favorable structures of a) Li, c) CO₂, and e) Li₂CO₃ adsorbed on N-6 site of pyridinic and graphitic N-doped CNT (002) surface. The brown, grey, green, and red balls represent C, N, Li, and O, respectively. Charge density difference of b) Li, d) CO₂, and f) Li₂CO₃ adsorbed on N-6 site of pyridinic and graphitic N-doped CNT (002) surface, respectively. The blue and pink regions represent the charge accumulation and charge loss, respectively. The isosurface value is set to be 0. 001 e Å⁻³. The electronic density of states (e-DOS) around the Fermi-level (*E*_f) of N-CNT after g) Li and h) CO₂ were adsorbed on the surface.

 Li_2CO_3 can be fully decomposed, allowing the release of CO_2 and storing electricity again. Interestingly, it is eye-catching that the N-Q and N-6 peaks dramatically decline to a negligible level after discharging and unexpectedly recover after recharging, while the N-5 peak remains stable during the entire discharge/ charge process (Figure 5i,j). It indicates that the doped pyridinic N and graphitic N atoms may provide a faster electron transfer path so that reactants can easily diffuse into these active sites, receive electrons, and generate massive Li2CO3 covered on the surface. Therefore, because of the obstruction of Li₂CO₃, the N-Q and N-6 peaks are more difficult to be detected by the surface-sensitive XPS. On the contrary, discharge products are less likely to be formed on the pyrrolic N-rich region, thus making N-5 peak available in the spectrum. The reappearance of N-Q and N-6 peaks after charging further verifies the reversibility of Li₂CO₃ as the discharge product in these Li–CO₂ batteries using N-CNTs as catalyst.

2.3.2. Computational Results

First-principle calculations on basis of DFT have been subsequently implemented to illustrate the advantages of introducing N-doping into CNTs from the perspective of theoretical simulations. Considering that pyrrolic-N (N-5), pyridinic-N (N-6), and graphitic-N (N-Q) dominate those doped N atoms, the models of one-layered graphite ((002) plane) doped with two groups of N atoms (N-6 + N-Q, N-5 + N-Q) were established to analyze the underlying physicochemical behaviors of Li,

 CO_2 , and Li_2CO_3 , with the results shown in Figure 6 and Figures S20 and S21 (Supporting Information). The adsorption energy is defined as $E_{ads} = E_A + E_S - E_T$, where E_T is the total energy of the corresponding system with specified atom or molecule adsorbed; E_A and E_S represent the energy of the specified atom or molecule and the pristine system, respectively. To read conveniently, all of the obtained adsorption energies are listed in Table 1 As can be seen from Figure 6a and Figures S20a and S21b (Supporting Information), Li atom is easier to stay steadily at the center of the defect induced by N-6 doping (2.500 eV) compared with the sites created by N-5 (1.77 eV) and N-Q (0.101 eV) in N-doped CNT, while Li atom is favorably adsorbed on the hollow site of hexagonal arrangement in the case of CNT (1.378 eV, Figure S19a, Supporting Information) after the structure has been energetically optimized. The adsorption energy values of Li on CNT and N-CNT indicate that N-doping can enhance the capture ability of CNT to Li atoms. This statement is further proved by charge density difference shown in Figure 6b and Figure S19b (Supporting Information), where N-CNT exhibits the stronger and broader charge interaction between Li and catalysts than that of pure CNT. Analogously, introducing N-6 atoms is also effective for the adsorption of CO₂ gas molecule (0.254 eV for CO₂/CNT, 0.294 eV for CO₂/N-6-CNT), as presented in Figure 6c,d and Figure S19c,d (Supporting Information). The aforementioned evidences elucidate the vital role of N-6 atoms in accelerating the diffusion of Li and CO₂ into the active catalytic sites as well as facilitating the reaction kinetics of CO₂ fixing. However, when a CO₂ molecule is adsorbed on the N-5 site (Figure S21c,

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Table 1. Adsorption energies (eV) of Li, CO $_2$, and Li $_2$ CO $_3$ at CNT and N-CNT, respectively.

	E _{ads} (Li) [eV]	$E_{ads}(CO_2)$ [eV]	$E_{ads}(Li_2CO_3)$ [eV]
CNT	1.378	0.254	1.128
N-6	2.500	0.294	2.628
N-Q	0.101	-0.151	0.787
N-5	1.770	Repulsion	Repulsion

Supporting Information), the N-5 atom prefers to move to another pyridinic-like position (Figure S21d, Supporting Information) instead of staying at N-5 site steadily after structure optimization. The similar structural aberration also occurs during the Li₂CO₃/N-5-CNT simulation, as shown in Figure S21e,f (Supporting Information). These results suggest that the doped N-5 atoms are more likely to exclude the adsorption of CO₂, leading to few discharge products generating at these sites. It may also partially explain the reason why only N-5 peak retains its intensity in XPS spectra after discharging. Desipte the incompatibility caused by N-5, based on the adsorption energy of Li2CO3 molecule on N-6-CNT (2.628 eV) and CNT (1.128 eV), we still consider that Li₂CO₃ is thermodynamically easier to deposit on the surface of N-CNT (see Figure 6e; Figure S19e, Supporting Information). The pyridinic N atom is regarded as a bridge connecting N-CNT and Li2CO3 to facilitate the electrons transfer (Figure 6f).^[12,27,39,55] It is beneficial for the fast stabilization or degradation of discharge product, thus resulting in a superior rate performance of the N-CNTs@Ti electrode. In comparison, the charge interaction between CNT and Li₂CO₃ becomes weaker without the assistance of N bridge (Figure S19f, Supporting Information). In addition, the electronic density of states (e-DOS) illustrated in Figure 6g,h reveals that the metallic character of N-doped CNT can be retained even after Li and CO₂ are adsorbed on the surface, which provides fast electron transport for the CO₂ fixing and releasing processes, as a result. By contrast, the metallic character of pure CNT is relatively lower after the adsorption (Figure S19g-i, Supporting Information). Hence, it is believed that N-5 doping is detrimental to the deposition of Li₂CO₃ because of its boredom to CO₂ molecule and the effect of N-Q doping mainly lies in the promotion of electronic conductivity of CNT. Whereas, N-6 doping can make a disctinctly positive influence on improving the kinetics of CO₂RR and CO2ER, thereby enabling a significantly enhanced electrochemical performance of the Li–CO₂ battery with a N-CNTs@ Ti cathode. The above computations agreed well with some reported catalytic mechanisms for N-doped carbon materials, as well.^[67] Because of the larger electronegativity of N than that of C, N-doping can break charge neutrality and induce charge redistribution in carbon networks, which endows it with special electronic, magnetic, optical, and even catalytic properties. In particular, for CO₂-related catalytic process, CO₂ adsorption together with O=C=O cleavage can be generally promoted in N-doped sites due to the charge polarization of N-C bond. Meanwhile, some key intermediates toward thermodynamically favorable species become relatively stable under the assistance of doped N atoms through coordinative electron transfer, which reduces the energy barrier and hence facilitates the kinetics of both CO2RR and CO2ER. Nevertheless, different configurations of nitrogen may lead to different influence on catalytic activity, which has been witnessed by many previous reports.^[68] Combining the known theories with our simulation results, we proposed the following mechanism for N-doping enhanced catalytic effect in Li-CO2 batteries. Assuming that the function of Li⁺ is analogous to that of H⁺ in traditional electrocatalytic CO2 reduction reactions, pyridinic-N (N-6) should be the most efficient chemical state for prelinminary conversion of CO₂, followed by graphitic-N, on account of their lower free energy barrier when forming critical amorphous intermediate $C_2O_4^{2-}$ ·Li⁺ which is possibly the rate-determined step to generate Li₂CO₃ and C.^[38,56,65] In the subsequent charge process, electrons can be fast transported via those N bridges between carbon matrix and discharge products, allowing the breakage of chemical bonds and reversible CO₂ release. Besides changing the charge distribution of neighboring carbon atoms to enhance catalytic activity, graphitic-N is also beneficial for boosting the electroconductivity by contributing ≈ 0.5 electron per atom to the π delocalized electrons group of graphene or CNT.^[67] As for pyrrolic-N (N-5) which shows incompatibility to CO_2 in our computations, it may be adverse to reduce CO_2 to C₂ intermediates, thus blocking the following CO₂ reduction reactions in Li-CO2 batteries. However, it has to be admitted that although many efforts have been made to explore the catalytic mechanism of N-doped carbon materials, the definitive explanation is hard to be given even in conventional CO2 electrocatalytic reactions without the participation of Li⁺ at the present stage. More advanced characterization techniques and design strategies need to be developed to clarify the CO₂RR and CO₂ER mechanism in Li–CO₂ batteries.

3. Conclusions

In general, we report a novel binder-free and free-standing composite fiber where highly surface-wrinkled and N-doped porous CNT networks are tightly anchored on the surface of Ti wire through a modified FCCVD strategy. Benefitting from the synergistic effects of N-CNTs and metal wire, high performance and high flexibility are synchronously integrated into this composite fiber. It can deliver a high discharge capacity of 9292.3 mAh g⁻¹, an improved cycle stability, and an excellent rate capability when evaluated as Li-CO₂ battery cathodes. The as-obtained composite fiber was further employed to prepare a quasi-solid-state flexible fiber-shaped Li-CO₂ battery, which can maintain normal functions before and after bending. The results of experiments coupled with theoretical simulations show that the highly wrinkled nanotube walls possess abundant defects to bring in more nitrogen atoms doped in the CNTs, of which the N-6 sites can be the most efficient chemical state for preliminary conversion of CO₂ and act as an efficient bridge to impel fast electrons transfer between reactants and catalysts, thereby significantly facilitating the reaction kinetics of CO₂ reduction and evolution. This work provides a new design strategy to direct the preparation of flexible fiber-shaped electrode with high performance for 1D flexible energy storage device, contributing to the development of wearable consumer electronics toward ubiquity.

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4. Experimental Section

Synthesis of Fiber-Shaped N-CNTs@Ti Hybrid Fiber: All reagents were purchased from Sigma-Aldrich and used without purification. N-CNTs@ Ti fibers were synthesized through a modified FCCVD method. First, 1000 mg of imidazole $(C_3H_4N_2)$ and 150 mg of ferrocene $(Fe(C_5H_5)_2)$ were added into 20 mL of acetonitrile (CH₃CN) and the mixture was subsequently ultrasonicated for 1 min to obtain a homogeneous solution which was then placed in the front of a furnace tube. Next, Ti wires (length: 20–30 cm, diameters: 210 μ m), which were washed with ethyl alcohol and deionized water beforehand, were placed at the center of this furnace tube. Before the furnace was subjected to heat treatment. argon was introduced into the quartz tube at a flow rate of 200 sccm for 15 min to eliminate the remaining air. The furnace was heated to 850 °C at a rate of 30 °C min⁻¹. Once the furnace reached the desirable temperature, it was slid to the appropriate position where the above precursor solution located and kept at 850 °C for 15 min. During this FCCVD process, the gasified droplets were carried into the center of the furnace by argon carrier and enabled the in situ growth of N-doped CNTs networks on Ti surface. After the furnace was cooled down to room temperature naturally under the protection of Ar, N-CNTs@Ti composite fibers were obtained. In addition, other typical common metal wires, like Cu, Al, and Ni, can be also utilized as flexible substrates to fabricate the new kinds of N-CNTs@metal wire composite fibers.

Material Characterizations: Morphological and structural information were acquired by using SEM (Hitachi S-5200), TEM (Hitachi), XRD (D/max 2200/PC, Rigaku, 40 kV, 20 mA, Cu K α radiation). XPS analysis was collected at a XSAM 800 spectrometer using monochromatized Al K α -radiation at 14 kV. Raman spectroscopy was performed on micro-Raman 2000 system Renishaw, Britain) possessing a 10 mW helium-neon laser excitation source which can produce the laser with a wavelength of 633 nm. The Al Mesh (0.11100100 mm, 100 mesh, No. 01 8100, Nilaco Co. Ltd.) coated with Au nanoparticles (ALM@Au) cathode used for SERS was fabricated by sputtering Au on the surface of clean Al mesh at 4 Pa, 5 mA for 100 s in an air-plasma environment.

The Assembly of Li-CO2 Cells: The electrochemical properties of as-obtained samples were tested in CR2032 coin-type cells with several holes on cathode side to allow the permeation of CO₂ gas. CNT electrodes were prepared by homogeneously spraying the slurry on a carbon paper (TGP-H-090, Toray), which was produced by mixing the active material (CNT 90 wt%, on dry solids basis) and poly vinylidene difluoride (PVDF, 10 wt%) in N-methylpyrrolidone (NMP) solvent. After being dried at 80 °C overnight, these CNTs were uniformly coated on the Toray carbon paper with an average area loading of around 0.45 mg cm⁻². By contrast, N-CNTs@Ti fibers that were cut into pieces were directly employed as air electrodes to assemble Li-CO₂ batteries without the fussy preparation procedure of electrodes stated above. The linear mass loading of surfacewrinkled and N-doped CNT networks on Ti wire was $\approx 6 \ \mu g \ cm^{-1}$, and about 5 cm N-CNTs@Ti fiber with active materials mass loading of 30 µg was placed in each Li-CO₂ battery cell. The mass loading can be further promoted by repeating the cycles of in situ growth of N-CNT networks by FCCVD strategy. Carbon paper (TGP-H-090, Toray) served as gas diffusion layer. All of the Li–CO₂ battery cells were assembled in an argon-filled glove box (H₂O and O₂ < 0.1 ppm). The CNT or N-CNTs@Ti electrode and lithium foil (diameter: 16 mm, thickness: 0.6 mm) were separated by glass fiber filter paper (GF/D whatman). The electrolyte consisted of 1 M lithium bis(trifluoromethane sulfone)imide (LiTFSI) dissolved in tetraethylene glycol dimethyl ether (TEGDME). The as-prepared coin cells were sealed in a dried CO_2 -filled box for the following electrochemical measurements. CV was conducted on a CHI660D electrochemical workstation at a scan rate of 0.1 mV s⁻¹ over the potential window of 2.0–4.5 V versus Li⁺/Li. The galvanostatic discharge/charge measurements were carried out on a LAND CT2001A electrochemical workstation under different test parameters at room temperature. It should be pointed out that all the capacities were calculated based on the weight of CNTs or N-CNTs in air cathodes.

The Preparation of GPE: LiTFSI, TEGDME, poly(vinylidene fluorideco-hexafluoropropylene) (PVDF-HFP, average M_n of \approx 130 000), NMP (99.5%), 2-hydroxy-2-methyl-1-phenyl-1-propanone (HMPP, 97%), and trimethylolpropane ethoxylate triacrylate (TMPET, average M_n of ~428) were purchased from Sigma and used without further purification. All reagents were operated in an argon-filled glovebox with O_2 and H_2O content less than 1 ppm. In the first step, 2.4 g of LiTFSI was dissolved in 1.6 g of TEGDME to generate a transparent solution A. 4.0 g of NMP was mixed with 1.0 g of PVDF-HFP under continuous stirring until the mixture became homogeneous and viscous, which formed Solution B. 0.01 g of HMPP was introduced into 3.0 g TMPET by stirring to constitute Solution C. It needs to be emphasized that Solution C should be stored in a brown glass bottle under darkness before utilization. When assembling Li–CO₂ batteries, solutions A, B, and C were mixed together and stirred drastically for 5 min in darkness. The obtained ivory slurry was subjected to UV-light irradiation for 20 s to produce solidified GPE.

The Preparation of Fiber-Shaped Li–CO₂ Battery: The quasi-solidstate flexible fiber-shaped Li–CO₂ battery was fabricated as follows: In the first step, Ti wire was winded into a spring-like structure before the FCCVD process. The Li–CO₂ battery device with coaxial structure was fabricated through assembling the spring-like N-CNTs@Ti into GPE coated Li wire which served as a flexible substrate and counter electrode, simultaneously. The GPE was synthesized by a mixed-solution strategy described previously. Finally, the device was encapsulated by a heatshrinkable tube with abundant holes for protection.

Computational Method: The projector augmented wave formalism of density functional theory as implemented in the Vienna ab initio Simulation Package was used in the system energy and electronic structure calculations. Generalized gradient approximation in the form of Perdew-Burke-Ernzerhof was used as the exchange-correlation functional. In order to get a better picture of weak interactions between the molecular and graphene, a computationally cost-effective "optB86b-vdW" method was chosen for van der waals (vdW) interactions. The Gaussian smearing method^[4] was used, and the width of smearing was chosen as 0. 05 eV. The energy cutoff for plane-wave expansion of the projector augmented wave (PAW) is 400 eV. The optimized lattice constant of graphene is 2.47 Å, which is in good accordance with previous computational results and experiment data. The slab model is $5\times5\times1$ supercell containing 50 C atoms. In the vertical direction, a vacuum layer of 20 Å in thickness is introduced for all the surfaces. The Brillouin zone is sampled using Monkhorst-Pack scheme with a k-point mesh of $3 \times 3 \times 1$ in the Gamma-centered grids for the structural relaxation, and $9 \times 9 \times 1$ k-point mesh is used for the static calculations of all the systems. The structure relaxation is continued until the forces on all the atoms are converged to less than 0. 03 eV $Å^{-1}$.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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Keywords

fiber-shaped cathode, flexible, $\rm Li-\rm CO_2$ batteries, N-doped CNTs, surface-wrinkled

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