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Fabrication of Self-Entangled 3-D Carbon Nanotube Networks from Metal-Organic Frameworks for Li-Ion Batteries

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KEYWORDS: metal-organic framework, self-entangled carbon nanotube, pyrolysis, ethyne, lithium ion battery

ABSTRACT: Three-dimensional (3D) carbon nanomaterial assemblies are of great interest in emerging applications including electronic devices and energy storage because of their extraordinary high electrical conductivity, mechanical and thermal properties. However, the existing synthetic procedures of these materials are quite complex and energy-intensive. Herein, a facile approach is developed for fabricating a self-entangled carbon nanotube (CNT) network under convenient conditions (400 °C for 1 hour), breaking the critical limitations of the current available methods. The keys of forming such 3D CNT network are the fragmentation of the sacrificial MOFs into nano-sized particles, the reduction of metal elements in MOFs to highly active nanocatalysts by introducing hydrogen, and the supplement of external carbon source by

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2
3 introducing ethyne. In addition, the highly conductive 3D porous CNT network facilitates electron
4 transfer and provides an excellent platform for high-performance Li-ion batteries (LIB).
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8 9 INTRODUCTION 10

11 Since the first discovery by Iijima,¹ carbon nanotubes (CNTs) have attracted fascinated interests
12 of the scientific community as arguably the most elegant carbon allotrope.² The unique properties
13 such as high surface area, high electrical conductivity, noticeable mechanical strength and
14 chemical inertness make CNTs the promising candidates for gas storages, catalysis,
15 electrochemical applications and conversion devices.³⁻⁸ Among the various methods that have
16 been developed for the synthesis of CNTs, the metal catalyzed chemical vapor deposition (CVD)
17 is currently the most common method⁹ and generally requires high temperatures in the 600-1000
18 °C range. This thermal treatment not only consumes intensive energy but also precludes the use of
19 temperature-sensitive substrates. Hence, new technology for lowering the growth temperature is
20 currently the subject of much interest.^{2, 10-12}
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34 Recently, pyrolysis of metal-organic frameworks (MOFs) has emerged as a new pathway for the
35 synthesis of novel nanoporous carbons and been recognized as an effective approach for CNT
36 synthesis.¹³⁻¹⁹ In general these approaches were operated by heating a MOF precursor under inert
37 atmosphere and the CNT formation can be described as route A in Scheme 1, where a two-step
38 process of metal-reduction, followed by CNT growth was proposed.¹⁸ Firstly, the metal ions in
39 MOFs were reduced by hydrocarbon organic ligands, under high temperatures (> 450 °C, step-1).
40 In the second step, at an even higher temperature (> 700 °C), the generated metal center acts as the
41 catalyst for CNT growth and the organic linker plays the role of the carbon source.^{18, 20-24} Lou et
42 al. reported a crystalline CNT constructed hollow framework, where they found that introducing
43 10% H₂ could greatly lower the MOFs-pyrolysis temperature and was critical for CNT formation.¹⁴
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Mai et al. claimed that CNTs could be obtained via low-temperature ($>430\text{ }^{\circ}\text{C}$) pyrolysis of MOFs in Ar by extending the duration time to 8 hs.¹⁸ Very recently, Hu and co-workers reported an elegant synthesis of spontaneously woven graphitic carbon networks by pyrolysis of nanosized ZIF-67 crystals at $600\text{ }^{\circ}\text{C}$ for 5 h under N_2 protection.²³ They noticed that the crystal size of the sacrificial MOF particles should be less than 100 nm; otherwise, only discrete carbon particles are formed. Despite these great advancements in MOF-derived CNT materials, several issues still need to be addressed to advance its further applications: first, the fabrication temperature is still high and the duration is long ($> 5\text{ h}$); second, the CNT yield is very low compared to the amount of the metal in the MOF lattice (typically 10%~20%, see discussion in ESI), due to the insufficient carbon supplements from scarifying the organic linkers; third, discrete particles isolated from each other are the common product, leading to a high contact resistance between the particles and thus decreasing the electrical conductivity.²³ Albeit CNT networks with 3D structure had been obtained from nanosized MOFs,²³ the requirements on the sacrificial particle size need special synthesis (additives required, *e.g.* surfactants) which undoubtedly prohibit its widespread applications. Therefore, the synthesis of CNT-assembled 3D structure to overcome the above-mentioned issues in one system remains a formidable challenge. On the other hand, prevailing carbonaceous materials with low density, high mechanical strength, and high conductivity have attracted significant interest for application in the next-generation lithium-ion batteries (LIB).²⁵ In particular, several previous studies²⁶⁻²⁸ of CNTs have shown great potential as possible anodes of LIB. It has been thoroughly demonstrated that lithium ions can diffuse into stable sites within the graphene layers of MWCNT leading to high Li^+ capacity.²⁶

Scheme 1. Schematic illustration showing the two-step formation of CNTs by pyrolysis of metal-organic frameworks under inert gas protection (Traditional method, Route A) or active gas (This work, Route B). The violet dots present the formed Co particles. SEM images of (a) obtained by Route A, where ZIF-67 was heated at $900\text{ }^{\circ}\text{C}$ for 3 hours under N_2 protection, the red arrows show the formation of big metal particles; (b) ZCNT-400 obtained by Route B, this work.

In this study, we report a facile fabrication strategy for the self-entangled CNT networks, which breaks all the above-mentioned limitations. Based on analysis of the two-step CNT formation process (Scheme 1), we introduced hydrogen as reductant to facilitate the metal reduction in step 1, and ethyne (C_2H_2) as external carbon source for CNT growth in the second step. As shown in Scheme 1 route B, thermolysis of ZIF-67 in hydrogen could reduce Co^{2+} to Co^0 nanoclusters at the temperature as low as $300\text{ }^{\circ}\text{C}$ within one hour, at the meantime, the MOF architecture cracked into nanosized fragments. Upon a rapid increase of the temperature ($20\text{ }^{\circ}\text{C}/\text{min}$) to $400\text{ }^{\circ}\text{C}$ and simultaneous introduction of an external carbon source of ethyne, self-entangled multi-wall carbon nanotube networks was obtained within a few minutes. Detailed studies shown that the MOF skeleton, high content of H_2 , as well as ethyne were all crucial to get the 3D CNT networks. To our best knowledge, this is the first example of using MOFs as pre-catalyst for 3D CNT growth

with external reducing gas and carbon source, remarkably different from all existed processes for CNT growth and MOFs pyrolysis conditions. MOF derived products by general methods are mainly N-doped CNTs, with carbon source solely from MOFs, while here external carbon source is used, resulting in major changes to the CNT structure: 1) Nitrogen content is significantly low; 2) The CNT yield is much higher; 3) high graphitic level although grown under lower temperature and shorter time. These differences are key factors for improved LIB performance.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased from Sigma-Aldrich and were used as received. Acetylene (99.9%) was purchased from Airliquid Alkhafrh Industrial Gases.

Synthesis of ZIF-67.²³ 2-Methylimidazole (6.6 g) dissolved in 400 ml of methanol was quickly added to a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.5 g) in 400 ml of methanol with magnetic stirring. The mixture was then stirred for another 1 hour and aged overnight at room temperature. Separation by centrifugation and washing with methanol repeated three times gives the pink powder product of ZIF-67 that was then dried at 120 °C for 24 hours under vacuum.

Thermal pyrolysis of ZIF-67 under inert environment. ZIF-67 (approximately 20 mg) in a ceramic boat was loaded into a quartz tube located in a tube furnace, and the quartz tube was then sealed and degassed with Ar twice. After being vacuumed again, the quartz tube was filled with Ar and the flow rate was kept at 100 scc. The furnace was then heated to a desired temperature of X °C with a heating rate of 5 °C/min and was held at the desired temperature for 5 hours. The carbon product was labeled as ZC-X.

Thermal reduction of ZIF-67 by hydrogen. 20 mg ZIF-67 in a ceramic boat was loaded into a quartz tube located in a tube furnace, and the quartz tube was then sealed and degassed with Ar twice. After being vacuumed again, the quartz tube was filled with H_2 , and the H_2 gas flow rate

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3 was kept at 100 scc. The furnace was then heated to a desired temperature at a rate of 20 °C/min
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5 and was held for 1 hour. Then, the gas was switched to 120 scc Ar and the system was quickly
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7 cooled down by opening the cover of the furnace. Product was labeled as ZH-X.
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10 **Synthesis of ZCNT.** 20 mg ZIF-67 in a ceramic boat was loaded into a quartz tube located in a
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12 tube furnace, and the quartz tube was then sealed and degassed with Ar twice. After being
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14 vacuumed again, the quartz tube was filled with H₂, and the H₂ gas flow rate was kept at 100 scc.
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16 The furnace was then heated to a desired temperature at a rate of 20 °C/min and was held for 1
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18 hour, and then 10 scc C₂H₂ was flowed into the system for 15 min. Then, the gas was switched to
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20 120 scc Ar and the system was quickly cooled down by opening the cover of the furnace.
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24 **Synthesis of ZCNT-400.** ZIF-67 (20 mg) in a ceramic boat was loaded into a quartz tube located
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26 in a tube furnace and the quartz tube was then sealed and degassed with Ar twice. After being
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28 vacuumed again, the quartz tube was filled with H₂/C₂H₂ (99/1), and the gas flow rate was kept at
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30 99 scc H₂ and 1 scc C₂H₂. The furnace was then heated to 400 °C at a rate of 20 °C/min and was
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32 held for 1 hour at 400 °C. The gas was switched to 100 scc Ar, and the furnace was cooled down
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38 **Acid etching of ZCNT-400.** The ZCNT-400 sample was treated with HCl (37%) until no
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40 obvious green color could be observed and then was washed several times with water to remove
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42 the acid. Finally, the sample was dried at 200 °C in a vacuum for 48 hours. The product was labeled
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44 as ZCNT-400-AL.
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47 **CNT growth with Co(NO₃)₂/PVDF as a precursor.** Co(NO₃)₂·6H₂O (200 mg) and PVDF (500
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49 mg) were dissolved and mixed in DMF to form a viscous paste, and then the mixture was cast on
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51 a silicon wafer surface and dried to form a film. Then, the procedure described above for the ZCNT
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53 synthesis was applied.
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Characterization. Scanning electron microscopy (SEM) was performed using a field emission scanning electron microscope (FESEM, Zeiss Merlin). Transmission electron microscopy (TEM) images were obtained using a Titan ST microscope (FEI Co.). The powder X-ray diffraction (PXRD) measurements were performed using a Bruker D8 Advance X-ray diffractometer with Cu-K α radiation using a voltage of 40 kV, current of 40 mA, and step size of 0.01° at a scanning rate of 0.2 seconds/step. Fourier transform infrared spectroscopy (FTIR) was performed using a Nicolet 6700 Smart FTIR spectrometer in the range from 4000 cm⁻¹ to 600 cm⁻¹. The nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP®2420 gas sorption system. Scanning electron microscopy (SEM) was performed using a Quanta 200 FEG system. Raman spectroscopy measurements were conducted using a Horiba Aramis confocal microprobe Raman instrument with a He-Ne laser of $\lambda = 632.8$ nm. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos Axis Ultra DLD spectrometer using a monochromatic Al K α X-ray source of 1486.6 eV, and the binding energies were referenced to the C 1s peak (set at 284.8 eV). Thermogravimetric analyses (TGA) were carried out on a SDT Q600 TG-DTA analyzer under N₂ atmosphere at a heating rate of 5 °C min⁻¹ within a temperature range of 30–900 °C.

Conductivity measurement: Conductivity was measured by two-point currency-voltage method. In general, the powder was compressed into a pellet with diameter d , and thickness l . The electrical resistance R is calculated by measuring the current I and voltage U , $R = U/I$. The conductivity σ is calculated as: $\sigma = l/RA = l/R/(\pi d^2/4)$

Electrochemical tests. The electrodes were prepared by casting the slurry consisting of 70 wt% ZCNT-400-AL, 24% Super P carbon, 3 wt% Carboxymethyl Cellulose (CMC) and 3 wt% Polyacrylic acid (PAA) onto a copper current collector. 1M LiPF₆ solution in ethylene carbonate

(EC)/diethylene carbonate (DEC) (volume ratio of 1:1) acts as the liquid electrolyte. Electrochemical performances were studied using an Arbin instrument in the galvanostatic mode, employing 2032 coin cells with lithium foil as the anode and Celgard 3501 separator sheets. The cut-off voltage range is 0.05-3.0 V. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Biological VMP-3 workstation over the frequencies ranging from 0.01 Hz to 200 KHz and at an oscillating voltage of 5 mV. The total mass loading of the electrode was approximately 1 mg cm⁻². The battery assembly was performed completely in an argon-filled glovebox (MBRAUN) in which the moisture and oxygen content remain lower than 0.5 ppm.

RESULTS AND DISCUSSION

To understand the effects of hydrogen and ethyne during the metal catalyst formation (step-1) and CNT growth (step-2), respectively, we have varied the conditions with and without hydrogen or ethyne, and investigated the products by wide-angle PXRD (Figure 1) and electron microscopies (EM) (Figure 2). Firstly, the traditional thermolysis under Ar atmosphere (route A in Scheme 1) was applied for comparison. As expected, the ZIF-67 crystallinity and morphology were well-maintained after heating at 450 °C for 4 hours (Figures 1b and 2b, named as ZC-450), which is consistent with the thermogravimetric analysis (TGA) (Figure S1, ESI), indicating the high thermal stability of ZIF-67 under inert environment. An increase in the temperature to 750 °C for five hours resulted in crystallinity loss, particle size decrease and generation of many metal particles, together with CNT formation on the surface (Figure S2, ESI). Upon a further increase in the pyrolysis temperature to 900 °C, abundant of CNTs (named as ZC-900) were observed along with many metal particles with sizes ranging from a few nanometers to a few hundred nanometers (Figure 2c); meanwhile, only Co facets of (111), (200) and (220) were observed by PXRD, and no obvious PXRD peak of CNTs was detected (Figure 1c), due to the low fraction of the CNTs in this

sample.²⁹ In fact, the final product obtained was only 40 wt % of the loaded ZIF-67, whereas 68 wt % was cobalt (based on 27 wt % Co in ZIF-67). To better evaluate the yield, we define the R value as the mass ratio of the carbon material in final product to the raw ZIF-67; for example, the R value of ZC-900 is $0.4 \times (1 - 0.68) = 0.13$. In this system, organic linker in MOFs is the sole reductant and carbon source, fundamentally limited the reduction time and CNT yield, also as a result of insufficient supply of carbon source to protect the active metal nanoparticles, metal particles aggregation could happen.

Figure 1. PXRD of (a) ZIF-67; (b) ZC-450, ZIF-67 heated under Ar at 450 °C for 4 h; (c) ZC-900, ZIF-67 heated under Ar at 900 °C for 5 h, $R = 0.13$; (d) ZH-300, ZIF-67 heated under H_2 at 300 °C for 1 h; (e) ZCNT-1, heated under H_2 at 300 °C for 1 h, then H_2/C_2H_2 (90/10 scc) at 400 °C for 15 min, $R = 5.33$; (f) ZCNT-2, ZIF-67 heated under $Ar/H_2/C_2H_2$ (90/10/5 scc) at 500 °C for 2 h, $R = 3.25$; (g) ZCNT-400, ZIF-67 heated under H_2/C_2H_2 (99/1 scc) at 400 °C for 1 h, $R = 1.23$; (h) commercial CNT. The black arrows indicate the CNT peaks, red arrows indicate Co peaks.

When hydrogen atmosphere was applied (Scheme 1, route B), ZIF-67 particles were found partially cracked when heated at 250 °C for one hour (ZH-250, Figure 2d), and fully decomposed

at 300 °C for one hour (ZH-300, Figure 1d, 2e). PXRD shown that the Co ions had been fully reduced into metallic Co (Figure 1d). Interestingly, first, the MOF particles cracked into small fragments with diameter about 40 nm (Figure 2e); second, the organic residuals still surrounded the generated nanoparticles as evidenced by SEM-EDS elemental mapping images (Figure 2f). These are very important as the organic residual protection may prevent aggregation of the active metal nanoparticles by lowering the surface energy,^{23, 30-31} while nano-sized fragments are crucial for 3D network formation by generating abundant mechanically contacted interface, similar as the role of nanosized ZIF-67 reported by Hu et al..²³ To our delight, upon further annealing ZH-300 with 10 scc ethyne and 90 scc H₂ at 400 °C for 15 mins (defined as ZCNT-1), graphitic carbon networks were obtained with very high yield (R = 5.33). A large amount of undesired carbon black is observed (Figure 1e, 2g and S3 in ESI), most likely because the reactivity is too high. Upon improving the fabrication conditions, self-entangled CNT networks were obtained by heating ZIF-67 under 99/1 scc H₂/C₂H₂ mixture at 400 °C, named ZCNT-400 with an R value of 1.23 (Figure 1e and 2h).

Figure 2. SEM images of (a) ZIF-67; (b) ZC-450; (c) ZC-900; (d) ZH-250; (e) ZH-300; (f) Elemental mapping for ZH-300; (g) ZCNT-1; (h) ZCNT-400; and TEM images of ZCNT-400 (i) a single CNT; (j) local magnified (i); (k) magnified part of the multi-layers; (l) Scan TEM mapping of Co particles in the CNT network; (m) FFT diffraction, the sharp points represent the Co crystal, and the cycle bright halo represents the surrounding graphitic carbon; (n) HR-TEM image of Co particle.

The clean and unique 3D CNT network structure of ZCNT-400 prompted us to further characterize its properties in details. As shown in Figure 1g, the diffraction peaks at $2\theta = 25.8^\circ$ and 42.9° agreed very well with the profile of the commercial CNT (Figure 1h), corresponding to the (002) and (101) reflections of carbon, respectively, while the peaks at $2\theta = 44.4^\circ$, 51.7° , and 76.0° corresponding to the (111), (200), and (220) reflections of metallic Co suggested that all Co (II) in ZIF-67 were reduced to Co (0). The much lower intensity of Co (0) than carbon indicates

the high fraction of CNTs, which is consistent with the high R value. The Raman spectrum shown in Figure S8 (ESI) displays the characteristic D-band and G-band features of carbon nanotubes, centered at 1320 cm^{-1} and 1610 cm^{-1} , respectively. As compared to the commercial CNT, the much higher I_d/I_g intensity ratio (2.3 *Vs* 0.8) reveals the existence of abundant amount of defects in the ZCNT-400. Figure 2j shows the high resolution transmission electron microscopy (HRTEM) image of an individual CNT with a diameter of approximately 45 nm terminated with a metal particle. An inner channel of approximately 7 nm surrounded by multiple graphite layers is observed in the magnified image of the nanotube. The interlayer spacing was measured to be approximately 0.34 nm (Figure 2k), which matches well with the value for multiwall carbon nanotubes. Highly crystalline nanoparticles at the terminal of CNTs with sizes of approximately 8-20 nm are observed. The nanoparticle lattice (figure 2n) spacing of 0.25 nm matches well with the lattice constant of Co with the $P6_3/mmc$ space group. Interestingly, as observed by STEM-EDS mapping of the nanoparticles (Figure 2l), only a marginal amount of oxygen (the green dots) was detected on the surface, suggesting that the nanoparticles are metallic Co with minor oxidation. This phenomenon is quite different from the observations for the nanoparticles formed via thermal reduction of MOFs, where the Co nanoparticles were found to easily oxidize (Figure S6, ESI).²³ This is arguably because there is not enough carbon protection in the thermally reduced Co-carbon networks, and most of the nanoparticles are out of or close to the surface, while in ZCNT-400, the Co nanoparticles are covered well and are protected by the CNT graphite layers, with only a small terminal part exposed.

X-ray photoelectron spectroscopy (XPS) analyses were further conducted on ZIF-67, ZC-900, and ZCNT-400 and were compared to study the surface compositions and chemical states of the different carbon frameworks with cobalt.³²⁻³³ Survey scans show the C, N, O and Co elements

present in ZIF-67 and ZC-900 with relatively high intensity, while in ZCNT-400, only C and O were discernible (Figure 3a survey). This further confirms that the Co is mainly located inside the framework rather than on the surface. High resolution (HR) C1s spectra of the ZCNT-400 3D network (Figure 3b) shows an asymmetric peak shape that was deconvoluted into five peaks. The peaks with approximately 40.4% of the integrated intensity were centered at 284.5 eV, and the peaks with 27.6% of the integrated intensity were centered at 284.8 eV, corresponding to the C-C bonds with sp^2 hybridization and sp^3 hybridization, respectively. The high fraction of sp^2 -hybridized carbon indicates the high degree of graphitization. The subsequent peaks at 286.2 eV and 288.4 eV represent the C-O, C-OH and COOH functional groups.³⁴ The expected characteristic shake-up line related to the aromatic structures or the $\pi \rightarrow \pi^*$ (HOMO-LUMO) transition is also present at ca. 290.1 eV, reflecting the interaction of emitted photoelectrons with the π electrons.³⁵ Although not discernible in the survey scan, the Co signal was observed in HR Co 2p XPS spectra with a much lower intensity compared to that for ZC-900 (Figure 3c). After deconvolution, the predominant peak corresponding to metallic Co indicates that most of the Co nanoparticles are found in the metallic form rather than the oxide form. Compared to the ZC-900 sample obtained by high temperature thermolysis in Ar that shows a small but discernible peak assigned to Co-N, no peak could be obtained at the same position for ZCNT-400, indicating that metallic Co nanoparticle is the true catalyst and C_2H_2 is the sole carbon source for CNT growth.

Figure 3. (a) XPS survey of ZIF-67, ZIF-67 heated under Ar at 900 °C for 5 h and ZCNT-400; (b) C1s HR XPS of ZCNT-400, (c) Co 2p HR XPS spectrum of ZC-900 and ZCNT-400; (d) N₂ ads/desorption isotherms of ZCNT-400 (black) and after acid etching ZCNT-400-AL (red). Inset shows the pore size distribution of ZCNT-400-AL.

Nitrogen adsorption data measured at 77 K lead to type II isotherms (Figure 3d), which, when analyzed using the Brunauer-Emmett-Teller (BET) equation, give the specific surface areas of 250 m²/g and 375 m²/g for ZCNT-400 before and after acid etching (ZCNT-400-AL), respectively.³⁶⁻³⁷ These specific surface area values are in the range of the theoretical values for five-layer-CNTs (295-430 m²/g) but are higher than the values for the thicker multi-wall CNTs (<200 m²/g).³⁸ Since there are clearly more than 5 layers in ZCNT-400 as observed in the TEM images, the higher specific surface area in the experiment compared to the theoretical value indicates that there are

many defects or open tubes, and thus, the internal surface of the CNTs also contributes to the apparent surface area. Additionally, bundles are formed between the CNTs either because they grow in this configuration from the same Co catalytic nanoparticle, or due to van der Waals forces, also contributing to the specific surface area.³⁸ The different pore size distribution including 0.8 nm, 1.2 nm and 3-15 nm provides further support for this hypothesis.

To demonstrate the importance of the MOF support, $\text{Co}(\text{NO}_3)_2/\text{PVDF}$ composite was used instead of ZIF-67 for the same procedure. After a treatment with hydrogen at 400 °C for 1 hour, the red-brown color of the cobalt salt disappeared, indicating that the cobalt was reduced. Following the addition of 20 scc C_2H_2 for 20 min, however, neither CNT formation nor even graphitic carbon formation was observed (Figure S4, ESI), suggesting an inactive nature of Co from this composite. The ratio of the hydrogen in the environment is also important for the self-entangled CNT network formation, most likely by affecting the cracking of large MOF particles into nanosized fragments which is crucial for obtaining a 3D carbon network.²³ In a control experiment, ZIF-67 was heated under an $\text{Ar}/\text{H}_2/\text{C}_2\text{H}_2$ environment at 500 °C with a flow rate of 90/10/5 scc. Isolated particles with CNTs formed on the outer surfaces of the particles were obtained after 2 hours (ZCNT-2, Figure 1f, and S5 in ESI). All of these results and observations demonstrate the validity of our proposed mechanism presented in Scheme 1. A relatively robust porous sacrificial scaffold and high H_2 content environment are two key factors for cracking the large sacrificial particles into nanosized fragments, generating catalytic active centers, with which an external carbon source of C_2H_2 can be catalyzed to grow CNTs. Since the fragments are small during CNT formation, a 3D network can be formed following a mechanism similar to that

reported in previous work.²³ It is important to emphasize that introducing H₂ is advantageous not only due to breaking the limitation of the initial MOF size but also because it makes the catalyst more active, enabling a further reduction in the reaction temperature. On the other hand, introducing C₂H₂ provides enough carbon source to obtain a much higher yield ($R>1$) and faster kinetics.

Figure 4. Electrochemical performance of ZCNT-400-AL: (a) Nyquist plots; (b) Stability and the corresponding Coulombic efficiency at the constant current of 100 mA g⁻¹.

It is also known that suitable voids, conductivity, and mechanical strength are all important factors for improving the performance.²⁵ High conductivity (ca. 7×10^4 S/m) of the MWCNTs with self-entangled 3D continuous graphitic networks were measured by current-voltage curve method (Figure S9, ESI). An LIB was constructed and the electrochemical impedance spectroscopy (EIS) as well as its charge/discharge cycling stability at 100 mA g⁻¹ were measured to evaluate the charge-transfer ability and cycling performance. As shown in Figure 4a, a classical Nyquist diagram was obtained from the EIS measurements that is composed of two depressed semicircles at the range from high-frequency to middle-frequency and a rising line at the low frequency region. The semicircle at high frequencies is attributed to the solid-electrolyte interphase resistance (R_{SEI})

that is common for graphite anode materials. The charge transfer resistance (R_{ct}) at lower frequencies can be related to the ion diffusion in the electrode. A low R_{ct} value of $91\ \Omega$ suggests that such a self-entangled CNT 3D network facilitates charge transfer and provides high electrical conductivity that is beneficial for a high-performance LIB. Besides, the simulated circular (Figure 4a) is fitted well with the experimental result, interpreting that the resistance is exactly composed of R_{SEI} and R_{ct} . A long life (Figure 4b) of the ZCNT-400-AL obtained at a current of 100 mA g^{-1} , shows an initial specific capacity of 807 mAh g^{-1} and 570 mAh g^{-1} after more than 200 cycles with a Coulombic efficiency of approximately 98%, revealing the long-term stable reversibility of ZCNT-400-AL.

Conclusions

In conclusion, self-entangled 3D continuous MWCNT networks were successfully synthesized at low temperature ($400\text{ }^{\circ}\text{C}$) and short time (1 hour) in high yield. The key factors in the synthesis are the thermal reduction/fragmentation of MOFs with hydrogen gas and introducing additional C_2H_2 gas as the carbon source. Compared to the existing process, our strategy breaks the limitation of particle size of the sacrificial MOFs and significantly improves the yield, lowers the temperature and decreases the reaction time. The synthesized self-entangled 3D CNT network exhibits excellent electrical performance for LIB applications with high capacity and long cycling stability (>200 cycles). Considering the intense current interest in MOF derivatives via pyrolysis, most of which are obtained under inert gas protection, and the ever-growing demand for CNT materials, this study demonstrates the potential of using MOFs as pre-catalysts for CNT growth and electrochemical energy storage (EES) applications.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

TGA analysis of ZIF-67, SEM image of ZC-750, HRTEM images of ZCNT-1, SEM images of product with $\text{Co}(\text{NO}_3)_2/\text{PVDF}$ as precursor, SEM images of ZCNT-4, A composite mapping image of ZC-900, FTIR of ZCNT-400 and ZCNT-400-AL, Raman spectrums of a commercial CNT and ZCNT-400, The IV curve of ZCNT-400, Galvanostatic (dis-)charge profiles, PXRD of ZCNT-400 and ZCNT-400-AL, SEM of ZCNT-400-AL, A short discussion on CNT yield. (PDF)

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Notes

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