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Hierarchical Vine-Tree-Like Carbon Nanotube Architectures: In-Situ CVD Self-Assembly and Their Use as Robust Scaffolds for Lithium-Sulfur Batteries

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The assembly of different low dimensional nanomaterials with distinct physical and chemical properties to three-dimensional (3D) hierarchical nanostructures has always been a hot research since it combines the advantages of each component and even leads to the formation of advanced materials with unexpected properties for unique applications.^[1,2] For instance, the combination of one-dimensional (1D) carbon nanotubes (CNTs) and two-dimensional (2D) graphene induces the formation of a graphene/CNT hybrid structure with intrinsic dispersibility, high surface area, as well as extraordinary electrical conductivity for advanced energy storage.^[3] The hierarchical composites made of graphene/CNT and metal oxide/conductive polymer exhibit high capacitance as supercapacitor electrode and large discharge capacity as the electrodes of Li-ion batteries.^[4] Assembling of low dimensional nanomaterials into a well-designed and more efficient architecture to achieve a better property and performance is still a great challenge in material science and energy storage.

It is known that the vine-tree structure is widely observed in nature when the plant is with a growth habit of trailing or climbing stems. The vines use trees for growth rather than devoting energy in a lot of supportive tissue, enabling the vine to reach sunlight with a minimum investment of energy. The trees may also facilitate the transportation of nutrient substances. Such hierarchical vine-tree structures offer the synergy between the vines and trees as well as afford the maximum utilization of sunshine and limited soil and space, which could also be a promising universal architecture in both macro- and micro-worlds. Considering an electrochemical energy storage device, two basic requirements need to be satisfied for the electrode materials to achieve a high performance: i) the materials should provide large quantities of surface area and active sites to facilitate their adsorption or redox-reaction with the ions from the electrolyte; ii) there should be an efficient electron

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pathway to ensure the fast transfer of electrons from the active materials to the current collectors. Enlighten by the vine-tree structures in nature, a vine-tree-like nanostructure is expected to be with high efficiency for the adsorption and reaction of ions from the electrolyte as well as the transfer of electrons. This could lead to high-performance electrode materials for energy storage devices.

In this contribution, we proposed the concept of in-situ chemical vapor deposition (CVD) self-assembly of hierarchical vine-tree-like CNTs (VT-CNTs) and evaluated their applications for lithium-sulfur batteries. The reason we select CNTs as the model system is due to the fact that the CNTs are one of the most typical low dimensional building blocks during the past 25 years and have demonstrated impressive properties and commercial applications in lithium ion batteries and nanocomposites.^[5] Herein, single-walled CNTs (SWCNTs) are selected as the flexible 'vine' and multi-walled CNTs (MWCNTs) are employed as the rigid 'tree' for the fabrication of VT-CNT nanostructures. In order to achieve the direct growth of such VT-CNTs, catalyst nanoparticles (NPs) with bimodal size distribution are required, in which the catalyst NPs with smaller size are expected to catalyze the growth of SWCNT 'vine' while the larger ones facilitate the growth of MWCNT 'tree' simultaneously (Figure 1). This is based on the fact that the size of catalyst NPs plays a key role in the wall number and diameter of the CNTs.^[6,7] Therefore, layered double hydroxides (LDHs) were used as the catalyst precursors because of their ability to produce thermal-stable metal NPs with well controlled size and density due to the unique layered structure of LDHs and strong metal NP-support interaction.^[2,8-10] Besides, the calcination of LDHs leads to the formation of layered double oxides (LDOs) composed of metal oxides and spinel phases,^[9] which are expected to facilitate the formation of bimodal catalyst NPs due to they afford two different kinds of catalyst support. Formamide (CH₃NO) was employed as the promoter along with CH₄ for the CVD self-assembly of VT-CNT nanostructures. The O atoms from CH₃NO are expected to further tune the size distribution and reactivity of the catalyst NPs derived from LDHs; the N atoms from CH₃NO are expected to introduce the doping of nitrogen heteroatoms into the CNT nanostructures to further improve their electrochemical performance. The as-grown SWCNTs and MWCNTs are expected to self-organize into a vine-tree-like architecture in order to minimize their interfacial adhesion energy.^[11] The as-fabricated VT-CNTs demonstrated excellent electrochemical performance as cathode scaffolds for Li-S batteries.



Figure 1. Schematic illustration of the CVD self-assembly of CNTs into a vine-tree-like structure on flake catalysts.

In detail, FeMoMgAl LDHs were adopted as the catalyst precursors for the in-situ growth of VT-CNTs. The as-prepared FeMoMgAl LDHs were hexagonal flakes with a lateral size of ca. 1 µm and a thickness of ca. 10 nm (Figure S1a). The powder X-ray diffraction (XRD) pattern shown in Figure S1b revealed the well crystallization of the as-prepared FeMoMgAl LDH flakes. After calcination and reduction, large quantity of Fe NPs can be produced on the surface of the as-calcined FeMoMgAl LDO flakes.^[2,9,10] As shown in the high-angle annular dark-field - scanning transmission electron microscopy (HAADF-STEM) images, the as-produced Fe NPs are mono-dispersed and uniformly distributed on the FeMoMgAl LDO flakes reduced by H_2 with the presence of CH_3NO (Figure 2a). Notably, the Fe NPs exhibit a bimodal size distribution (Figure 2b). Some Fe NPs are with a size around 20 nm, while some other Fe NPs are with a much smaller size below 3 nm (as labeled by the red circles). Statistical analysis based on hundreds of the Fe NPs gives their bimodal size distribution (Figure 2c). It further demonstrates that almost 43% of the Fe NPs are with a size around 2 nm that facilitate the growth of SWCNTs, while the others are with a size concentrated between 10-25 nm that lead to the growth of MWCNTs.^[6]

After the CVD of CH₃NO and CH₄, CNT strands with a diameter of ca. 1 μ m can be observed on both sides of the ascalcined FeMoMgAl LDO flakes (Figure 2d). Further observation reveals that such 1- μ m CNT strands are consisted of large amount of smaller bundle-like CNT units. High-magnification scanning electron microscopy (SEM) image clearly indicates that these CNT units exhibit a vine-tree-like morphology, in which small-diameter CNTs wrap around the large-diameter CNTs (Figure 2e). There are a large amount of CNTs with diameters of tens of nanometers (the "tree") surrounding with some small-diameter CNTs (the "vine") in the as-grown CNT strands (Figure 2f). The high-resolution transmission electron microscopy (TEM) image (Figure 1g) reveals that the tree-like CNTs are composed of bamboo-like MWCNTs. The small-diameter

CNTs are mainly composed of highly defective SWCNTs. Rather than randomly entangled with each other, the SWCNTs herein exhibits a vine-like morphology wrapping around the MWCNTs. The self-assembly of the vine-tree-like structure can be ascribed to their trend to minimize the interfacial adhesion energy between SWCNTs and MWCNTs. In another aspect, the SWCNTs formed on tiny Fe NPs always grow much faster that the MWCNTs grown on large metal NPs.^[6,7,10,12,13] Therefore, the VT-CNT structures can also be considered as a result of matching the apparent growth rate of SWCNT 'vine' and MWCNT 'tree' in a similar rate from the FeMoMgAl LDO flakes.

Notably, the concentration of CH₃NO in the CH₃NO/CH₄ mixture played an important role in the efficient growth of the VT-CNTs. With the feeding rate of CH₄ fixed at 100 mL min⁻¹, the introduction of a small amount of CH_3NO (0.1 mL h⁻¹) into the reaction system induced the formation of long SWCNT strands (Figure S2). However, high quality interlinked SWCNTs and a small amount of short-aligned SWCNTs were available if no CH₃NO was introduced.^[6,7,12] Increasing the feeding rate of CH₃NO to 0.2 mL h⁻¹ led to the formation of VT-CNTs, whereas, the content of tree-like MWCNTs was too low to construct a perfect vine-tree-like structure (Figure S3). The growth of fascinating VT-CNTs was achieved by increasing the CH₃NO feeding rate to 0.5 mL h⁻¹ (Figure 2). A higher concentration of CH₃NO (1.5 mL h⁻¹) resulted in the formation of well aligned N-doped MWCNTs (Figure S4). It was also found that if CH₃NO (3.0 mL h^{-1}) was applied solely as carbon source without CH₄, no CNTs but only NPs were formed (Figure S5). Therefore, the co-feeding of CH₃NO and CH₄ with a proper CH₃NO concentration is a key point for the successful growth of the VT-CNTs. It was found that the CVD of CH₄ on large-size Fe MPs (>5 nm) embedded on LDO flakes preferred to form graphitic carbon encapsulated Fe NPs rather than MWCNTs and resulted in their deactivation.^[6] Herein, the robust growth of MWCNTs on Fe NPs with large size can be ascribed to the existence of 'O' from CH₃NO, which was important for preserving the reactivity

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Figure 2. (a, b) STEM images of the catalyst NPs formed on the FeMoMgAl LDH flakes reduced by H_2 and CH₃NO for 5 min at 950 °C and (c) their bimodal particle size distribution; SEM images of (d) the CNT bundles and (e) an obvious vine-tree-like CNT assembly grown from the FeMoMgAl LDH flake with co-feeding of CH₃NO and CH₄; the inserted image in (e) shows an optical image of the gourd vines wrapping around a bamboo; (f) TEM, (g) high resolution TEM images, and (h) Raman spectrum of the as-grown VT-CNT assembly; (i) The N1s XPS spectra of VT-CNTs.

of large-size Fe NPs. It is widely accepted that the introduction of weak oxidant, such as CO_2 and H_2O , can significantly promoted the growth of SWCNTs by modulating the reactivity and size distribution of catalyst NPs.^[14] Herein, the CH₃NO decomposed into CO and NH₃ as soon as it was introduced into the CVD system at a high temperature of 950 °C. The CO was inferred as the key component that reduced the calcined LDH and tuned the size distribution and activity of the as-produced catalyst NPs from LDHs and, thus, leading to CNTs with different kinds of structures. The NH₃ is the main component for the doping of nitrogen heteroatoms, leading to the formation of N-doped VT-CNTs.

Strong radial breathing mode peaks were detected in the Raman spectrum for the as-grown VT-CNTs with a CH₃NO feeding rate of 0.5 mL h⁻¹, indicating the existence of large amount of SWCNTs (Figure 2h).^[15] The I_D/I_G ratio for the VT-CNTs was 0.46, much larger than that of SWCNTs and even graphene/SWCNT hybrids grown from LDH-derived catalysts.^[6,7] This further demonstrated the high defect density of the SWCNTs in the VT-CNTs. The thermogravimetric analysis (TGA) result under oxygen atmosphere revealed that

the as-grown VT-CNTs had a carbon purity of 95.3 wt%, corresponding to a high yield of 21.9 g_{VT-CNTs}/g_{cat} (Figure S6). Two weight loss peaks located at ca. 480 and 532 °C were observed in the TGA profile, which correspond to the oxidation of vine-like SWCNTs and tree-like MWCNTs, respectively. This indicated the mass ratio of SWCNTs and MWCNTs in the VT-CNT architecture was around 2.6 : 1. An amount of ca. 1.2 wt% for the N doped in the VT-CNTs was determined by the X-ray photoelectron spectroscopy (XPS), with chemisorbed-, quaternary-, and pyridinic-N as the three main components (Figure 2i and S7). Attributed from the high graphitization degree of SWCNTs, the quantity of N-doping is not very high.^[16] The content of O is with a high value of 6.7 wt%, especially when compared to the carbon nanomaterials obtained by CVD of CH4 on LDH based catalysts at a temperature of 950 °C (Figure S7).^[16,17] Such a high content of O can be a reason for the high defect density of the as-grown VT-CNTs.

Li-S batteries were strongly considered in this research to evaluate the electrochemical performance of VT-CNTs due to their ultra-high specific energy density (2600 Wh kg⁻¹), assuming the complete reaction between lithium and sulfur to





form $\text{Li}_2 S.^{[18,19]}$ The preparation of carbon nanomaterials with unique structures and morphologies as cathode materials for Li-S batteries has been extensively studied.^[19–21] CNTs are considered as one of the most promising cathode materials for Li-S batteries because of their remarkable electrical conductivity and excellent mechanical properties. Their electrochemical performance can be further improved when the CNTs are assembled into aligned form, especially for the vertically-aligned CNTs directly connected to the current collector.^[22] However, the low specific surface area (<200 m² g⁻¹) of MWCNTs limits their capability to accommodate sulfur at high loading amount and poor cycling stability for the MWCNT/S cathodes.^[23,24] The situation becomes much better for SWCNTs due to their much larger surface area (>1200 m² g⁻¹) and the mesoporous structure originated from the interspaces among SWCNT bundles.^[25] However, the SWCNTs are usually entangled with each other, which degrades their ability in the construction of efficient conducting networks.

Herein, the rational combination of MWCNT frameworks and SWCNTs with large surface area into a hierarchical vinetree-like nanostructure is expected to be promising candidate for high performance Li-S cathode materials. A simple

melt-diffusion process was conducted to infiltrate sulfur into the porous structure of the VT-CNTs. Figure 3a shows the TEM image and energy-dispersive X-ray spectroscopy (EDXs) mapping results of the as-fabricated VT-CNT/S nanocomposites. A uniform distribution of sulfur in the VT-CNTs was demonstrated. TGA result revealed a high sulfur loading of ca. 60 wt%, with much better thermal stability than pure elemental sulfur. This indicated the strong interaction between sulfur and the VT-CNTs (Figure 3b). The as-prepared VT-CNTs exhibited a high mesopore volume of 1.5 cm³ g⁻¹ and a small micropore volume of 0.05 cm3 g-1. After the infiltration of sulfur, most of the mesopores and all of the micropores were occupied by sulfur (Figure 3c). The specific surface area of VT-CNTs decreased from 649.3 to 60.5 m²/g after the incorporation of sulfur. No intrinsic peak of elemental sulfur can be detected in the XRD spectrum of the VT-CNT/S nanocomposites compared to that of pure VT-CNTs, further indicating the uniform distribution of sulfur in the frameworks of VT-CNTs.

Li-S cells were assembled to test the performance of the VT-CNT/S cathodes. Two typical plateaus at around 2.3 and 2.1 V for Li-S batteries in the discharge curve of the VT-CNT/S cathode were observed at a current density of 0.2 C (1.0 C = 1672 mA g^{-1})



Figure 3. (a) TEM image and EDXs mappings of the VT-CNT/S nanocomposites; (b) TGA profiles of the VT-CNT/S nanocomposites; (c) Pore size distribution and (d) XRD spectra of the VT-CNTs before and after the infiltration of sulfur.



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(Figure S8a). In addition, a small plateau at around 1.8 V, which was widely observed for the reduction of sulfur incorporated in micropores,^[26] was also observed. This plateau can shift to much lower potential at a higher current rate of 1.0 C due to the strong polarization. Therefore, the charging and discharging process of the VT-CNT/S cathodes was also operated in a wider voltage range of 1.0-3.0 V in spite of the typical range of 1.7-2.8 V to fully utilize the incorporated sulfur. The cyclic voltammogram (CV) profiles conducted in both of the two potential ranges exhibited typical anodic/cathodic peaks for Li-S batteries (Figure S8b and S8c). An additional weak anodic peak at around 1.5 V was also observed in the CV test with the voltage window of 1.0-3.0 V (Figure S8d). Except for the first cycle of initial activation, no obvious changes on the anodic/cathodic peaks can be observed during the following four cycles for the CV profiles conducted in both 1.0-3.0 and 1.7-2.8 V, indicating the high electrochemical stability of the cathode.

The cycling stability of the VT-CNT/S cathodes was illustrated in **Figure 4**a. An excellent cycling stability was achieved when the charge/discharge process was conducted in the potential range of 1.7–2.8 V. It is well accepted that the performance of Li-S cells is affected by a number of factors, such as areal sulfur loading, current density, the composition and amount of electrolyte.^[21,22] To have a more appropriate comparison, SWCNT/S and MWCNT/S cathodes with similar sulfur loading amounts (~60 wt%) were prepared and tested in a similar process with that of VT-CNT/S composites. It was observed that the VT-CNT/S cathodes performed much better than that of SWCNT/S and MWCNT/S cathodes (Figure 4a) A high capacity of 680 mAh g⁻¹ per sulfur was preserved after 100 cycles with an initial value of 844 mAh g^{-1} at 1.0 C (Figure S9 and S10a). Even after 450 cycles, the capacity was still retained as a high value of 530 mAh g⁻¹, indicating a capacity decay of ca. 0.08% per cycle (Figure 4a and Figure S10a). A much higher initial reversible capacity of ca. 1210 mAh g⁻¹ per sulfur was achieved at 1.0 C for the 1.0-3.0 V charge/discharge potential window, which decreased to ca. 600 mAh g⁻¹ after 100 cycles, indicating a 50% capacity decay (Figure S9 and S10b). After 450 cycles, only ca. 20% of the initial capacity can be maintained with a value of 230 mAh g⁻¹ (Figure S10b). Such an unstable cycling performance was ascribed to the more serious irreversible oxidation of sulfur active materials due to the over charge.^[27] A stable coulombic efficiency above 95% was achieved for the cvcling processes conducted in both 1.0-3.0 and 1.7-2.8 V. This phenomenon can be further confirmed by the charge-discharge profiles shown in Figure 4b. As is shown that there was an obvious increase in the polarization and continuous drop of capacity within initial 50 cycles when the Li-S cells were conducted between 1.0-3.0 V. However, more stable electrochemical behavior can be achieved with even charge/discharge plateau voltages if the charge-discharge process was conducted in the potential range of 1.7-2.8 V.



Figure 4. (a) Cycling profiles of the VT-CNT/S, SWCNT/S, and MWCNT/S cathodes with a voltage window of 1.7–2.8 at a current rate of 1.0 C; The inset image show the illustration of VT-CNT/S cathode during discharge/charge cycle, in which the vine-like SWCNTs provide large surface area and abundant porous structure for the storage and confinement of sulfur/polysulfides, and the tree-like MWCNTs render a robust mechanical structure and electronic conductive pathway; (b) Charge-discharge profiles of the VT-CNT/S cathode in the voltage window of 1.7–2.8 V and 1.0–3.0 V at a current density of 1.0 C; (c) The rate performance of the VT-CNT/S cathode between 1.0–3.0 V.

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The VT-CNT/S cathodes also exhibited more excellent rate performance compared to that of MWCNT/S and SWCNT/S composites (Figure S11). When tested in the potential range of 1.0–3.0 V, a high discharge capacity of 1418 mAh g^{-1} based on sulfur was achieved at a current density of 0.5 C for the VT-CNT/S cathodes. The capacity reduced gradually with the increasing charging current density. A capacity of 997 and 630 mAh g⁻¹ can still be preserved at a high current density of 3.0 and 4.0 C, respectively (Figure 4c). The capacities based on the whole cathode materials were also calculated, which reduced from a high value of ca. 770 to 340 mAh $g_{\text{electrode}}{}^{-1}$ when the current density increased from 0.5 to 4.0 C. Such excellent rate performance was also achieved when the Li-S cells was tested in the potential range of 1.7-2.8 V. A discharge capacity of ca. 1120 mAh g⁻¹ per sulfur was achieved at 0.1 C, and capacities above 1000 mAh g⁻¹ can still be retained until the current density increased to 0.5 C. At a high current density of 4.0 C, the capacity was still maintained at ca. 570 mAh g⁻¹ (Figure S11). The recovery of a reversible capacity of ca. 860 mAh g⁻¹ was achieved at 0.5 C directly following the charge/discharge process at the high current rate of 4.0 C. It did not return to the original value due to the reasonable capacity decay during the long cycling process at different current densities.

The excellent rate and cycling performance of the VT-CNT/S cathodes were ascribed to the hierarchical structure of the VT-CNTs. Compared to MWCNTs, the vine-like SWCNTs afforded large quantity of porous structure and higher surface area for the uniform physical absorption and confinement of sulfur rather than a simple physical coating of sulfur on the MWCNT surfaces. This played an important role in the storage of sulfur and suppressing the shuttling effect of the as-generated polysulfides, leading to a much better performance than the aligned MWCNT/S nanocomposites.^[28] The tree-like MWCNTs in VT-CNTs rendered robust electron pathways to ensure a good rate performance.^[25] The electrochemical impedance spectroscopy (EIS) data shown in Figure S12 demonstrated the good conductivity and stability of the VT-CNT/S cathodes. The slight increase in the charge transfer resistance after deep cycling might be caused by the formation of passive layer on carbon frameworks during the charge-discharge processes. Besides, the high defect density of the vine-like SWCNTs with oxygencontaining functional groups can facilitate stronger interactions between the polysulfides and SWCNTs.^[29] Furthermore, the doping of N atoms into the nanocarbon frameworks may also help in enhancing the affinity between sulfur, polysulfides and the nitrogen-doped carbon scaffolds.^[24,30] As a result, the VT-CNTs can serve as much better cathode materials for Li-S batteries than MWCNTs and SWCNTs.

In summary, an in-situ self-assembly of VT-CNTs has been achieved by CVD of a CH_3NO/CH_4 mixture on the catalyst NPs with a bimodal size distribution derived from FeMoMgAl LDHs. The VT-CNTs are composed of vine-like SWCNTs wrapping around the tree-like MWCNTs. The concentration of CH_3NO is a key point for the successful growth of VT-CNTs due to its important role in the size distribution and reactivity of catalyst NPs generated from FeMoMgAl LDHs. N-doping is also achieved on the VT-CNT architecture due to the introduction of N atoms from CH_3NO . The as-fabricated VT-CNTs exhibit excellent rate performance and cycling stability as



cathode scaffold materials for Li-S batteries due to the following facts: i) the vine-like SWCNTs provide large surface area and an abundant porous structure for the storage and confinement of sulfur/polysulfides; ii) the tree-like MWCNTs render a robust mechanical structure and electronic conductive pathway; iii) the doping of nitrogen as well as the oxygen-containing functional groups on VT-CNTs facilitate the chemical absorption of sulfur/ polysulfides. We can foresee the promising applications of the VT-CNTs in other electrical energy storage devices, such as fuel cells, solar cells, supercapacitors, and Li-ion batteries. This work also provides a general biomimetic strategy toward the design of hierarchical nanomaterials with extraordinary electron pathways as well as tunable surface/interface that can be used in areas of catalysis, separation, drug delivery, and energy conversion and storage.

Experimental Section

Catalyst Preparation: The FeMoMgAl LDH catalysts were synthesized using a typical urea assisted co-precipitation reaction. Fe(NO₃)₃•9H₂O, Na₂MoO₄•2H₂O, Mg(NO₃)₂•6H₂O, Al(NO₃)₃•9H₂O, and urea were dissolved in 250.0 mL deionized water with [Fe³⁺] + [Mg²⁺] + [Al³⁺] = 0.15 mol L⁻¹, n(Fe) : n(Mg) : n(Al) : n(Mo) = 0.4 : 0.04 : 2 : 1, [urea] = 3.0 mol L⁻¹. The solution was then left to stand at 94.0 °C for 12.0 h in a 500.0 mL flask, which was equipped with a reflux condenser in ambient atmosphere. The as-obtained suspension was filtered, washed by deionized water and freeze-dried to get the final products of FeMoMgAl LDHs.

One-Step Self-Assembly of VT-CNTs: The VT-CNTs were prepared using a catalytic CVD with FeMoMgAl LDH flakes as the catalyst precursors and methane/formamide as carbon/nitrogen feedstocks. In detail, 0.50 g LDH flakes were distributed uniformly on a quartz boat which was then placed at the center of a horizontal guartz tube. The guartz tube was then inserted into a furnace and heated from room temperature to 950 °C under flowing Ar (100 mL min⁻¹). When reaching the reaction temperature, a mixture of CH_4 and H_2 was introduced into the reactor with a flow rate of 100 and 50 mL min⁻¹, respectively. The formamide (CH₃NO) was also introduced into the reactor simultaneously with its feeding rates (0.10, 0.20, 0.50, 1.5, and 3.0 mL h^{-1}) controlled by an injector fixed with a high-precision pump. The CVD growth was maintained for 30 min at 950 °C before the furnace was cooled to room temperature under Ar and H_2 protection. The reduction of the FeMoMgAl LDHs was carried out under a similar process with a mixture of H₂ (50 mL min⁻¹) and CH₃NO (0.5 mL h⁻¹) at 950 °C for 5 min. The as-grown products was collected and purified by routine HCl (5.0 mol L^{-1}) and NaOH (13.0 mol L^{-1}) treatment.

Structural Characterizations: The morphology of the samples were characterized using a JSM 7401F (JEOL Ltd.) SEM operated at 3.0 kV and a JEM 2010 (JEOL Ltd.) TEM operated at 120.0 kV. The HAADF-STEM was obtained on Titan 80-300 which operated at 300 kV. XRD patterns were recorded on a Bruker D8 Advance diffractometer equipped with a Cu-K α radiation source. TGA was performed under heating at 10 °C min⁻¹ using a Mettler Toledo TGA/DSC-1 analyzer. The growth yield of VT-CNTs was obtained by TGA under oxygen atmosphere. The sulfur loading of the VT-CNT/S nanocomposites was determined by TGA under N₂ atmosphere. Raman spectra were obtained with a Horiba Jobin Yvon LabRAM HR800 Raman spectrophotometer excited at 633 nm. The pore size distributions and Brunauer-Emmett-Teller (BET) specific surface areas of the samples were calculated based on the guenched solid density functional theory (QSDFT) method from the N₂ sorption isotherm collected by an Autosorb-IQ2-MP-C system. The XPS spectra were obtained using X-ray photoelectron spectroscopy conducted on an Escalab 250Xi.

Electrochemical Performance of VT-CNT/S Cathodes for Li-S Batteries: The VT-CNT/S nanocomposite was prepared by a melt-diffusion



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strategy. Typically, the VT-CNT/S was first mixed with sulfur powder by milling. The mixture was then placed in a sealed Teflon container at 155 °C for 4.0 h to incorporate the sulfur into the porous structure of the VT-CNTs. Two-electrode cells in the form of standard 2025 coiltype cells were constructed in an Ar-filled glove box to evaluate the electrochemical performance of the VT-CNTs as cathode materials for Li-S batteries. The VT-CNT/S cathode slurry was prepared by mixing the VT-CNT/S nanocomposites (90%) and poly(vinylidene fluoride) (PVDF) binder (10%) in an N-methylpyrrolidone (NMP) solvent dispersant. Positive electrodes were produced by coating the slurry onto aluminum foil, which were then dried at 60 °C for 24.0 h and cut into circular pieces with a diameter of 12 mm. The areal density of the sulfur in the electrode was in the range of 1.0-1.5 mg cm⁻². The MWCNT/S and SWCNT/S electrodes were prepared through a similar process. A solution of 1.0 mol L⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in 1,3-dioxolane: 1,2-dimethoxyethane (1 : 1 v/v)was employed as the electrolyte. Approximately 20 µL of electrolyte was used in the fabrication of each Li-S cell. Lithium metal foil was used as the negative electrodes, and polypropylene membranes from Celgard, Inc. were used as separators. The coin cells were tested in galvanostatic mode at various currents within the voltage ranges of 1.7-2.8 and 1.0-3.0 V using a Neware multichannel battery cycler. The cyclic voltammogram at a scan rate of 0.1 mV/s and electrochemical impedance spectroscopy measurements were performed on a Solartron 1470E electrochemical workstation with the amplitude of 5 mV and frequency range of 10^{-2} – 10^{5} Hz. A current density of 1672 mA g⁻¹ (1.0 C) based on the mass of sulfur, which is equivalent to full discharge or charge in 1 h, was applied in both current sweep directions.

Supporting Information

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

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