

# Stretchable single-walled carbon nanotube double helices derived from molybdenum-containing layered double hydroxides

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## ABSTRACT

Single-walled carbon nanotube (SWCNT) double helices were fabricated with directly synthesized FeMoMgAl layered double hydroxide flakes as the catalyst precursor. The as-obtained SWCNT double helices were closely packed, while the screw pitches of the double helices were tunable from 2 to 10  $\mu\text{m}$ . Straight millimeter-length SWCNT yarns can be obtained by further stretching the SWCNT double helices.

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Three-dimensional (3D) micro-coiled or nano-coiled carbon materials have attracted extensive attentions because of their unique conformations and outstanding mechanical and electromagnetic properties, which endue them to be potential candidates for absorbers of electromagnetic waves or cosmic rays, micro sensors, micro actuators, electrode materials, etc. [1–6]. The combination of two congruent helical coils with the same axis or differing by a translation along the axis leads to the formation of a double-helix structure, which is the basic structure of deoxyribonucleic acid (DNA). Carbon materials in double-helix structure are attractive due to their unexceptional properties originating from the accurate self-organization of the two helical carbon coils [7–9]. The preparation methods of double helical carbon micro-coiled fibers were established by chemical vapor deposition (CVD) [9,10]. However, the large diameter, rigidity and disordered graphene layers of carbon fibers limited the complete utilization of the mechanical and electronic properties of these helical carbon materials.

With superior electronic, mechanical, and thermal properties, carbon nanotubes (CNTs) were a promising building block for double helical structure. Very recently, we reported the fabrication of double/multi-walled CNT double helices using transition metal (Fe, Co) based layered double hydroxides (LDHs) as the catalyst precursors [8]. Compared with double/multi-walled CNTs, single-walled CNTs (SWCNTs) afford better mechanical, thermal and electrical properties, and exhibit wide applications in high-performance nanocomposites and high electron mobility for electronics. To achieve the fabrication of SWCNT double helices, a chemical precursor mediated process by intercalating  $\text{MoO}_4^{2-}$  into FeMgAl LDHs was used to lower the catalyst particle size and improve its den-

sity. SWCNT double helices were successfully synthesized on the  $\text{MoO}_4^{2-}$  intercalated FeMgAl LDHs [11]. However, the as-used chemical precursor mediated process to prepare the  $\text{MoO}_4^{2-}$  intercalated FeMgAl LDHs was very complicated and time-consuming. In this letter, we explore the idea that Mo-containing LDHs were directly synthesized to fabricate the SWCNT double helices with good extension characteristics.

The Mo-containing FeMoMgAl LDH flakes ( $n(\text{Mg}):n(\text{Al}):n(\text{Fe}):n(\text{Mo}) = 2:1:0.4:0.04$ ) were directly synthesized using a urea assisted co-precipitation reaction with  $\text{Na}_2\text{MoO}_4$  as the additive since  $\text{MoO}_4^{2-}$  can be used as a kind of charge-balancing anion for LDHs. Unlike the chemical precursor mediated process [11],  $\text{MoO}_4^{2-}$  here was intercalated among the LDH layers in the competition of  $\text{CO}_3^{2-}$ , and both of the two anions existed in the interlayer spaces of the as-prepared LDHs. The scanning electron microscopy (SEM) image of the FeMoMgAl LDHs illustrated the hexagonal flakes with a lateral size of ca. 1  $\mu\text{m}$  and a thickness of tens of nanometers (Fig. 1a). Powder X-ray diffraction (XRD) pattern (Fig. 1b) indicated that the FeMoMgAl LDHs possessed a good crystallinity and the lattice parameters were  $a = 0.304$  nm and  $c = 2.286$  nm. X-ray fluorescence (XRF) was utilized to determine the composition of the FeMoMgAl LDHs, and the molar ratio of Fe to Mo was confirmed to be 10:1. Thus, the formula of the as-prepared FeMoMgAl LDHs can be represented as  $[\text{Mg}_{0.53}\text{Al}_{0.30}\text{Fe}_{0.17}(\text{OH})_2][(\text{CO}_3)_{0.22}(\text{MoO}_4)_{0.015}] \cdot n\text{H}_2\text{O}$ .

A large amount of FeMoMgAl LDH flakes served as both the substrates and catalyst precursors, and they were firstly calcined into layered double oxide (LDO) flakes during the heating process. After the reduction of the LDO flakes for 5 min, Fe nanoparticles with a size ranging from 1 to 5 nm and a density of ca.  $5 \times 10^{15} \text{ m}^{-2}$  embedded on LDO flakes were obtained

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(Fig. 2a and b). The as-obtained Fe nanoparticles were with excellent thermal stability attributed to the pinning effect of Mo around the Fe nanoparticles [11], which provided high density catalysts for continuous growth of aligned SWCNTs. Besides, the plate-like morphology of the LDO flakes was well preserved after the reduction. After the introduction of a carbon source, aligned SWCNTs synchronously grew and extended perpendicularly from both sides of the FeMoMgAl LDO flakes (Fig. 3a and b). With the continuous growth of the SWCNT arrays, the array tips met space resistance attributed from the neighboring flakes or SWCNT arrays. In order to minimize the stresses associated with the growth of SWCNTs, the arrays started to twist and coil on themselves around the ultra-light LDO flakes ( $\sim 0.2$  ng), leading to the further assembly of SWCNT double helices with a length of tens of micrometers and a diameter of several micrometers (Fig. 3c).

The as-obtained SWCNT double helix exhibited a close-packed structure with the LDO flake on the tip, which connected the two SWCNT strands on both sides (Fig. 3d–f). In addition, the closely packed SWCNT double helix was flexible. When pulling the tip of the double helix by tweezers with

tiny tip under an optical microscope, the screw pitch was stretched from 2 to 10  $\mu\text{m}$  (Fig. 3g and h). With further stretching, even straight SWCNT yarn with a diameter of 1–2  $\mu\text{m}$  can be obtained (Fig. 3i). The two SWCNT yarns on both sides of the LDO flakes can be separated from each other (Fig. 3g), and the length of the SWCNT yarn was calculated to be ca. 1.4 mm if the double helix was fully unfolded. Because the catalyst site was always on the tip of the micrometer-scale double helices, the growth of SWCNTs in this model can conquer the carbon source diffusion and release the mechanical stress during the growth of SWCNT array. Thus, the double helical structure is a potential platform for the direct fabrication of super-long SWCNT yarns. Furthermore, if the as-grown SWCNTs in the double-helix structure carried a high current, the double helical SWCNTs can be further modulated as a prototype for nanoelectromagnetic Faraday coils for nano-electro-mechanical systems.

The SWCNTs on both sides exhibited strong interaction with the LDO flake, and even strong ultrasonication for 1440 min can not damage the connection between the SWCNT strands and the LDO flake (Fig. 4a). Meanwhile, the

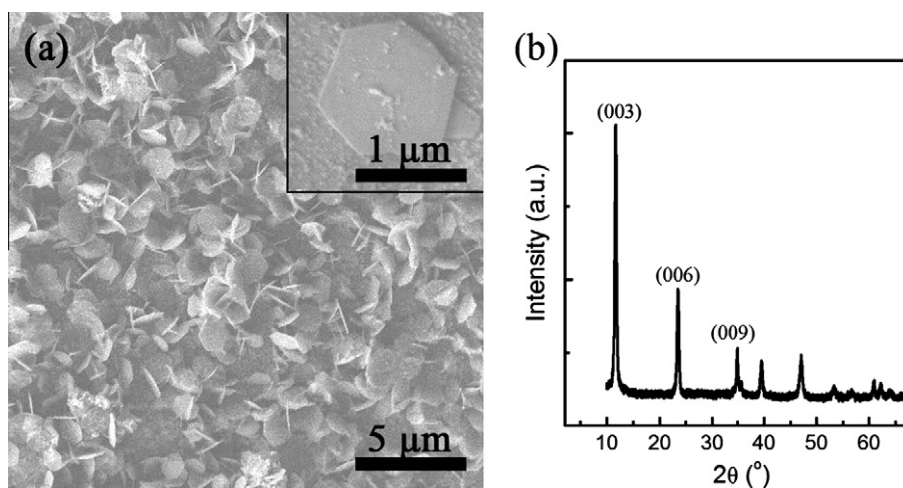


Fig. 1 – (a) SEM image of the FeMoMgAl LDH flakes, inserted SEM image clearly shows a hexagonal FeMoMgAl LDH flake; (b) XRD pattern of the FeMoMgAl LDH flakes.

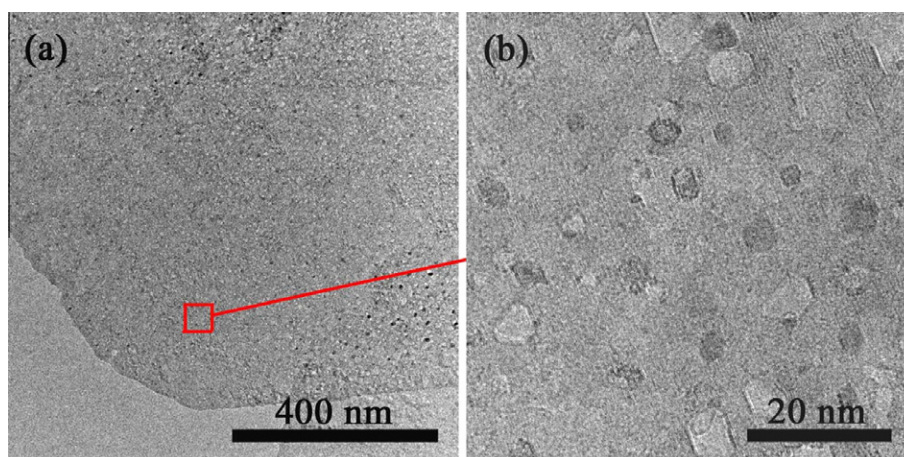
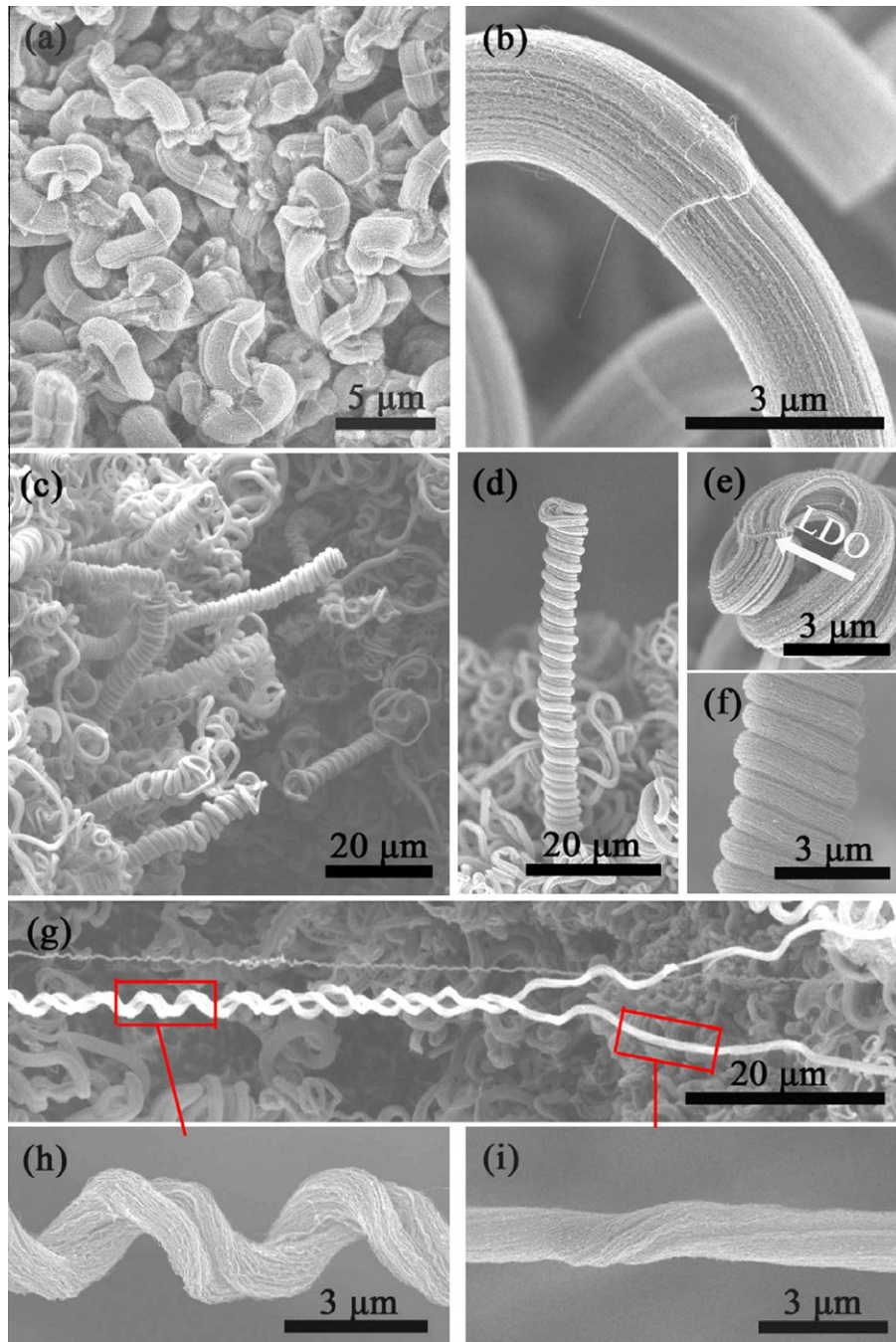


Fig. 2 – (a) TEM and (b) high resolution TEM images showing the Fe nanoparticles embedded on the FeMoMgAl LDO flakes after a 5-min reduction.

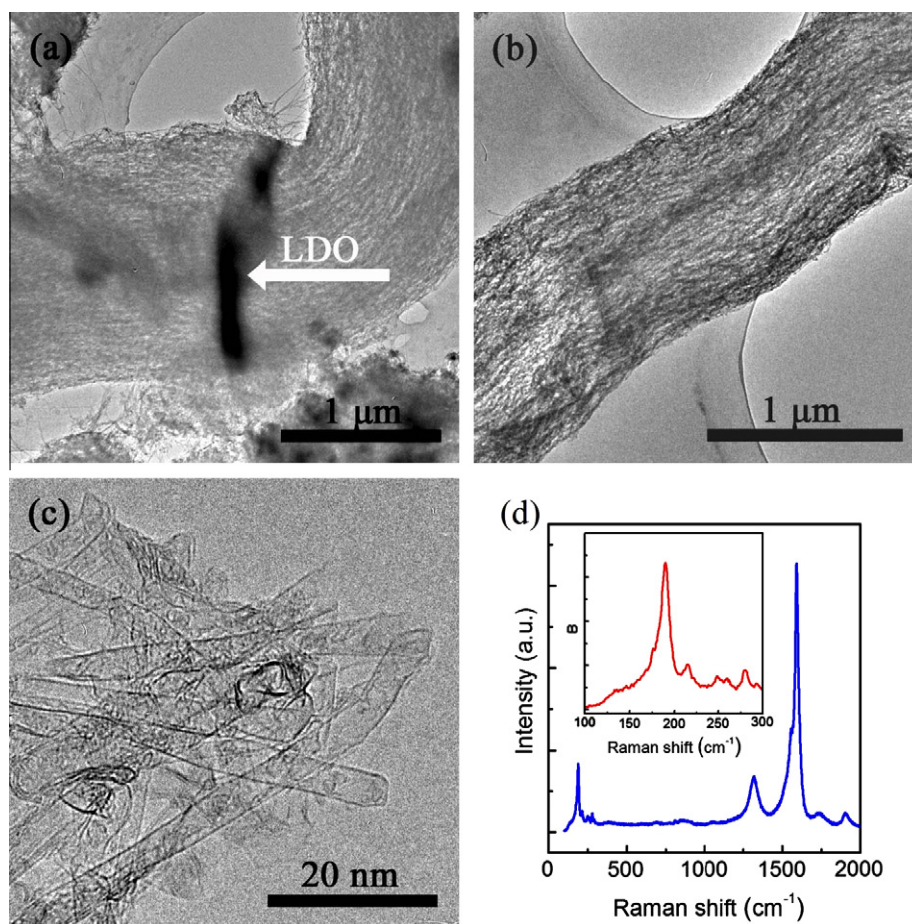
aligned array morphology was also well preserved (Fig. 4b). The high resolution transmission electron microscopy (TEM) image presented in Fig. 4c clearly showed the structure of the SWCNTs in the SWCNT double helices. Strong radial breathing mode peaks and a low  $I_D/I_G$  ratio from Raman spectra illustrated in Fig. 4d macroscopically indicated SWCNTs were obtained on FeMoMgAl LDH flakes.

In summary, 3D SWCNT double helices were fabricated by hierarchical assembly of SWCNTs through direct CNT growth

using Mo-containing LDHs as the catalyst precursor. This is an easy route to build 3D double helical nanoarchitectures by bottom-up self-assembly strategy between one-dimensional SWCNTs and two-dimensional flakes. The screw pitch of the double helix was tunable from 2 to 10  $\mu\text{m}$ , and straight SWCNT yarn in millimeter length can be obtained by further stretching of the SWCNT double helices, indicating the good extension properties of the SWCNT double helices. This work provides a structural platform towards the design of hierar-



**Fig. 3** – (a and b) SEM images showing the SWCNT arrays grown on both sides of FeMoMgAl LDH flakes after a 5-min reaction; SEM images showing (c) SWCNT double helices derived from FeMoMgAl LDH flakes after a 1-h reaction, (d) an as-grown SWCNT double helix and (e) its top section with a piece of LDO flake, as well as (f) the middle section with the twisted SWCNT strands; (g–i) SEM images showing a stretched SWCNT double helix.



**Fig. 4** – TEM images showing (a) the connection between the SWCNTs and the FeMoMgAl LDO flake and (b) a single SWCNT strand after strong ultrasonication for 1440 min; (c) The high resolution TEM image showing the structure of SWCNTs; (d) Raman spectrum and the RBM peaks (the inserted image) of the as-grown SWCNTs.

chical materials that can be used in areas such as high-performance CNT yarns, nanoelectronics, magnetic devices, and energy conversion.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2011.01.020.

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## Direct electrochemical attachment of carbon nanotubes to carbon fiber surfaces

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### ABSTRACT

A novel electrochemical grafting of carbon nanotubes (CNTs) on the surfaces of carbon fibers using water as dispersive medium was achieved by the electrolysis of carboxylic acid-functionalized CNTs. The resulting CNT-hybridized carbon fibers showed a selective distribution of CNTs at active carbon sites on the fibers associated with the edge graphite layers and defects, without destroying the crystalline structure of carbon fibers. Such hybridized fibers should provide a potential for improving the mechanical properties of advanced composites by increasing the load transfer at fiber/matrix interfaces.

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The carbon nanotube (CNT)-hybridized carbon fiber has now been an interest of research for its unique combination of properties (e.g. mechanical and electrical properties), cost-effective and scalability [1–3]. Such type of fibers can be benefited from the macro-reinforcement provided by the traditional carbon fibers and the complementary reinforcement on the nanoscale provided by the CNTs. Electrophoretic deposition of functionalized CNTs onto epoxy-sized carbon fiber surfaces is reported to fabricate the hybridized carbon fibers [2,4]; however, the weak adhesion between carbon fibers and the sized epoxide may injure the interfacial shear strength and bending properties of composites even after oxidative treatment of carbon fiber surfaces [5,6]. Moreover, some methods for CNT-reinforced carbon fibers [1], e.g. in situ growth of CNTs on carbon fiber surfaces by thermal chemical vapor deposition, have shown a significant reduction in tensile strength of carbon fibers for using high-temperature treatment and metal catalysts, which in turn is detrimental to mechanical properties of composite parts. Few studies have been performed regarding the electrochem-

ical bonding of CNTs on carbon surfaces because the carbon-carbon bonds in CNTs are too strong to break even after the CNTs are introduced to carbon surfaces. In this work, a novel electrochemical process to graft carboxylic acid-functionalized CNTs on carbon fiber surfaces using water as dispersive medium was demonstrated, which establish a foundation for further studies, i.e., preparation of hybridized fiber reinforced composites that exhibited strong interfacial shear strength and bending strength.

The carbon fibers used were polyacrylonitrile-based unmodified and unsized high-strength carbon fibers (Institute of Coal Chemistry, Chinese Academy of Sciences, China) with the following specified properties: tensile strength 3800 MPa, elastic modulus 230 GPa, density 1760 kg/m<sup>3</sup>, diameter 7 μm. The multi-walled carbon nanotubes (95% purity, 20–60 nm) were purchased from Shenzhen Nanotech. Port. Co. Ltd. (Shenzhen, China). A three-electrode system of a Model LK98BII Electrochemical Analyzer (Lanlike Co. Ltd., Tianjin, China) was established with a carbon fiber bundle used as the working electrode (positive), and a graphite sheet, and

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