HIERARCHICAL ARCHITECTURES BASED ON ONE-DIMENSIONAL CARBON NANOTUBES AND TWO-DIMENSIONAL LAYERED DOUBLE HYDROXIDE FLAKES

Qiang Zhang[1], Meng-Qiang Zhao, Jia-Qi Huang, Fei Wei

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
[1] Present address: Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, D-14195 Berlin, Germany
E-mails: zhang-qiang@mails.tsinghua.edu.cn (Q. Zhang); zhaomq04@gmail.com (M.Q. Zhao); hjq03@mails.tsinghua.edu.cn (J.Q. Huang); wf-dce@tsinghua.edu.cn (F. Wei).

Combining materials with one-dimensional (1D) nano-wire/nanotubes and two-dimensional (2D) lamellar flakes leads to three-dimensional hierarchical nanocomposites with unexpected properties for unique applications. For instance, the combined three-dimensional composites clay-polymer and clay-carbon nanotube (CNT) nanocomposites show extraordinary mechanical and energy absorbing properties. The key issue for a successful application of nanocomposites lies in the ability of manipulating the arrangement of the two phases (filler and matrix) into a well designed structure. Up to now, CNTs can be controllably synthesized on various kinds of matrices to directly fabricate hierarchical nanocomposites. Compared with traditional procedures, the in situ nanocomposite fabrication strategy is quite easy-operating and low cost. However, in these studies just multi-walled CNTs (MWCNTs) can be synthesized on the certain matrix to in situ fabricate nanocomposites. It should be noticed that single/double walled CNTs (S/DWCNTs) are with much more ideal structure, such as smaller diameter, larger aspect ratio and lower defect density. Compared with MWCNTs, S/DWCNTs exhibit better mechanical, thermal and electrical properties, and find wide applications in high-performance nanocomposites, high electron mobility for electronics, and field emission display. If the one-dimensional S/DWCNTs can be controllably synthesized on two-dimensional flakes to fabricate a hierarchical composite, a kind of novel advanced functional material with good dispersion of S/DWCNTs will be obtained.

Recently, layered double hydroxides (LDHs), also known as hydrotalcite-like materials, which are a class of two-dimensional nanostructured anionic clays whose structure is based on brucite ($Mg(OH)_2$)-like layers, can be controllable synthesized easily in large scale. Most metals, such as Fe, Co, Ni, Cu, Zn, Mg, Al, Ca, and Li, can be arranged in the lamellar LDH flake at an atomic level with controllable component. This is attributed to the substitution of divalent metal cations by trivalent cations within their hydrotalcite-like layers, which leads the LDH layer to be positively charged and balanced by a wide variety of anions within their interlayer domains. Compared with natural clay, the composition of LDHs is much simpler and can be anticipated, these are very important for actual catalysts, catalyst precursors, or catalyst supports. After the calcination and reduction, metal particles can be produced and they are uniformly distributed on flakes, which are good catalysts for CNT growth. A few reports have described the in situ growth of CNTs on LDHs. However, only random MWCNTs with a diameter ranging from 10 to 50 nm and a specified surface area of less than 50 m^2/g were synthesized in most cases. Compared with MWCNT growth, high temperature and small catalyst particles are needed for S/DWCNT growth. Thus the composition of LDH flakes and the growth window should be delicately explored. Moreover, the morphology of LDHs after growth was few mentioned and the performance of composites with CNTs and calcined LDH (c-LDH) flakes were not full investigated.

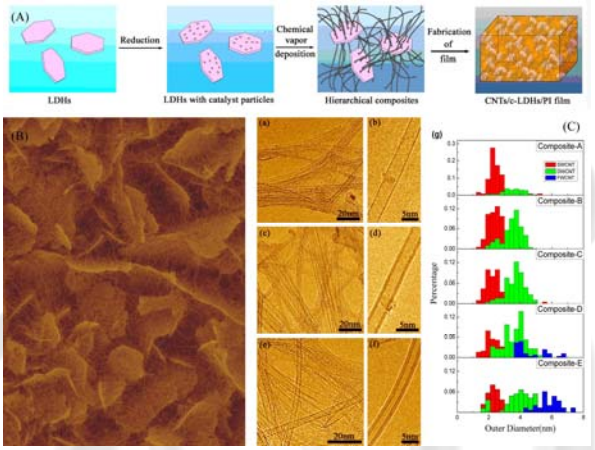

Fig. 1 (A) The schematic illustration showing the procedure for construction of the hierarchical composites of single/double walled carbon nanotubes interlinked LDHs and incorporation of CNT/c-LDHs hybrid filler into PI matrix to make the CNTs/c-LDHs/PI film. (B) SEM image of the obtained hierarchical composites; (C) TEM and HRTEM photograph of CNTs in (a,b) Composite-A, (c, d) Composite-C, (e, f) Composite-E; (g) Distribution of outer diameter for obtained S/D/FWCNTs in Composites A-E [1].

Here, we used Fe/Mg/Al LDHs, as well as Co/Mg/Al, Ni/Mg/Al and Co/Fe/Mg/Al LDHs as the catalyst precursor, and explored the idea of in situ fabrication of S/DWCNTs interlinked with lamellar flakes forming directly a three-dimensional hierarchical nanocomposite. As shown in Fig. 1, the LDHs were used as the two-dimensional lamellar flakes for CNT growth. After calcinations and reduction, metal particles with small sizes can be produced. With the introduction of carbon sources, a well controlled CNT interlinked hierarchical nanocomposite was obtained. The lamellar structure of LDHs could be preserved; moreover, they are individually distributed among the entangled S/DWCNTs. The synthesized CNTs showed large SSA value, little defects, and high yield. The combination of the one-dimensional CNTs and two-dimensional c-LDH flakes promoted the CNT

dispersion. The diameter and wall number of the CNTs can be easily tuned by changing the proportion of iron in LDHs. Lower iron content of LDHs favored the growth of SWCNTs for its trend to form large amount of catalyst particles smaller than 3 nm. While for higher iron content, catalyst particles with a size ranging from 3 to 5 nm were more likely to be formed to synthesize DWCNTs. An interlinked CNT layer alternating with lamellar flakes structure can be obtained after the compression of the hierarchical composites. The mechanical properties of CNTs/c-LDHs/PI films were significantly improved compared to neat PI.

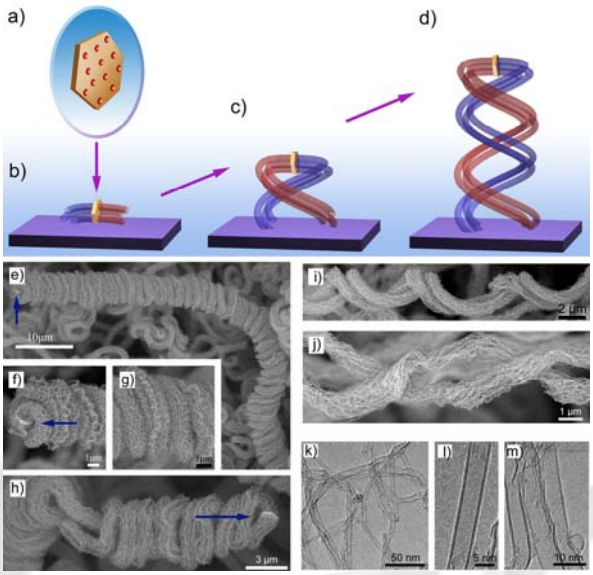

Fig. 2 Illustration of the formation of CNT array double helix. A Fe(Co)/Mg/Al LDH flake was provided as the substrate. After calcination and reduction, metal particles were uniformly formed on each side as shown in (a). With the introduction of hydrocarbons, CNT arrays were opposite grown on the both side of the flake (b). The growth site was at the root of CNTs attached on the calcined LDH flakes, with catalyst particles sitting on the end. The growth of CNT arrays from LDH flakes is free to grow in such a way as to minimize the stresses associated with the growth of a CNT arrays. Thus, when the CNT array tips met space resistance, they still continuously grew from the LDH flake via coiling on themselves into a CNT array double helix (c). With continuous growth and twisting, a super long CNT array double helix was formed, as illustrated in (d). (e) A dextrorotatory double-helix CNT arrays grown on a LDH flakes; (f) and (g) show the calcined LDH flakes and middle section of (e). (h) A levorotatory double helix grown on a LDH flake; Stretched (i) a levorotatory and (j) a dextrorotatory CNT array double helix.(k) TEM and (l,m) high resolution TEM of double walled CNTs grown on a single Fe/Mg/Al LDH flake.

Moreover, we used the 1D CNTs and 2D LDH flakes to fabricate CNT array double helices. Helix is a geometric motif which can be found both in natural and artificial structures. Helicity can be observed in the spiral arms of galaxies or in microscopic structures such as right- or left-handed quartz as well as in human art and architecture. Double helical structure, which consists of two congruent helices with the same axis or differing by a translation along the axis, is the basic structure of deoxyribonucleic acid (DNA). Using CNT as a promising building block for single/double helical structure always provides novel platforms to demonstrate the superior electronic, mechanical, and thermal properties of 1D nanomaterials. Great efforts have just been made to study single helical carbon nanofibers and nanotubes because of their coiled morphologies and potential applications. Up to now, single helical CNTs are generally synthesized as by-products in the catalytic decomposition of organic substances over transition metal catalysts or their alloys. The synthesis of CNT array double helix, similar to organic forms found in nature, remains a challenge for scientists.

Generally, the formation of double helix structure requires self organization of two strands with one end as the node. If aligned CNTs are oppositely grown on a single flake, then the two strands may coil on themselves around the flake and twist into a double helix. Based on this consideration, we explored the idea of bottom-up growth of aligned CNTs on a LDH flake to form a CNT array double helix directly. Our concept involved a facile CVD growth of CNT array double helix on a LDH flake, as illustrated in Fig. 2. After CVD growth, there were close packed dextrorotatory (Figure 2e-g) and levorotatory (Figure 2h) helical CNT strands, in both of which CNT arrays are uniformly twisted with each other. A flake can be found at the end of each CNT array double helix (arrowed in Figure 2f,h), connecting the two CNT stands. The as grown CNTs were self-organized into CNT array double helices. Moreover, the screw pitch of the dextrorotatory (Figure 2f) and levorotatory (Figure 2g) double helix can be stretched from 3 to 10 μm. The structure of CNTs in the double helix can be easily modulated by varying the active sites on the flakes. Typical TEM images of the as-grown CNT products in the double helix grown on LDH flakes were illustrated in Fig. 2k-m, if Fe/Mg/Al (0.4:2:1) LDHs were used as catalysts, double walled CNTs (>95 %) with an inner diameter of 4-6 nm were synthesized. More details, such as structure modulation and properties, can be found in Ref. 2.

In summary, a novel facile route to build 3D nanoarchitectures via bottom-up self-organization between 1D nanowires/nanotubes and 2D flakes/films was provided. This is suitable for large scale production. This work also provides a structural platform towards the design of hierarchical materials that can be used in areas such as nanoelectronics, magnetic devices, catalysis, separation, and energy conversion.

References

[1] Zhao MQ, Zhang Q, Jia XL, Huang JQ, Zhang YH, Wei F. Hierarchical composites of single/double walled carbon nanotubes interlinked flakes from direct carbon deposition on layered double hydroxides. Adv Funct Mater 2010;28(4):677-95.

[2] Zhang Q, Zhao MQ, Tang DM, Li F, Huang JQ, Liu BL,et al Carbon nanotube double helix. Angew Chem Int Ed. 2010, doi: 10.1002/anie.200907130.