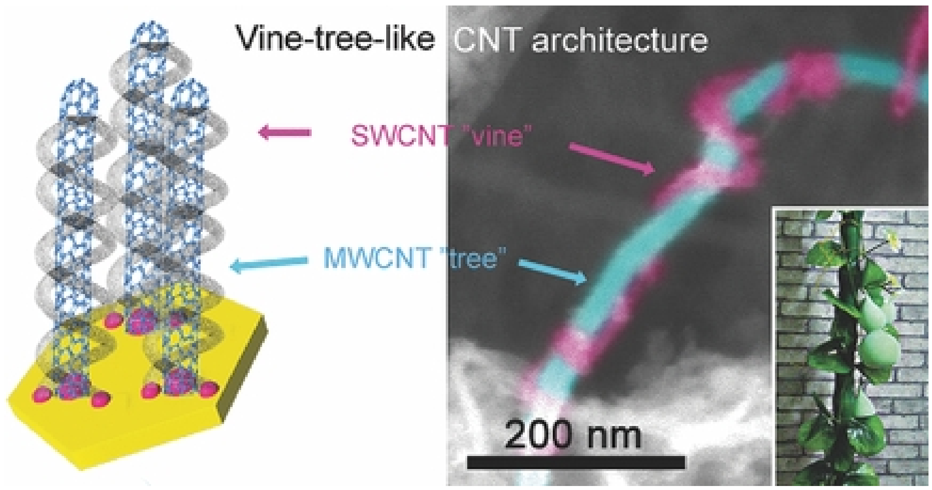
Vine-tree-like CNT architectures

November 3 2014



Hierarchical vine-tree-like carbon nanotube architectures composed of vine-like single-walled carbon nanotubes wrapping around the tree-like multi-walled carbon nanotubes are fabricated through in-situ chemical vapor deposition self-assembly. The vine-tree-like nanoarchitectures exhibit excellent cycling stability and rate performance when employed as the cathode scaffolds for lithium-sulfur batteries.

The vine-tree structure is widely observed in nature when the plant has a growth habit of trailing or climbing stems. The vines use trees for growth rather than devoting energy to development 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 synergy between the vines and trees as well as the maximum utilization of sunshine and limited soil and space, which could also be a promising universal architecture in both macro- and micro-worlds.

The combination of low dimensional nanomaterials with distinct physical and chemical properties into three-dimensional (3D) hierarchical nanostructures is a hot research topic due to the advantages of each component and suggest the formation of advanced materials with unexpected properties for unique applications. A vine-tree-like nanostructure is expected to have 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.

New work by Prof. Qiang Zhang and Fei Wei's research group in Department of Chemical Engineering at Tsinghua University (China) reports on the in-situ self-assembly of vine-tree-like nanostructure using carbon nanotubes (CNTs) as the building blocks by chemical vapor deposition (CVD). 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, and energy conversion and storage.

By using catalyst nanoparticles (NPs) with a bimodal size distribution during the CVD synthesis, scientists have obtained vine-tree-like CNTs (VT-CNTs) that are composed of vine-like single-walled CNTs (SWCNTs) wrapping around the tree-like multi-walled CNTs (MWCNTs). The VT-CNTs, described in the journal of *Advanced Materials* in the Volume 26, Issue 41, Page 7051-7058, Published on November 5, 2014 ('Hierarchical Vine-Tree-Like Carbon Nanotube Architectures: In-Situ CVD Self-Assembly and Their Use as Robust Scaffolds for Lithium-Sulfur Batteries') could serve as excellent cathode scaffolds for high-performance 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 of the past 25 years.' Qiang Zhang, an Associate Professor in Tsinghua University, tells Phys.Org, 'The formation of bimodal catalyst NPs is the most important factor. This is because the size of catalyst NPs plays a key role in the wall number and diameter of the CNTs. The catalyst NPs with smaller size are expected to catalyze the growth of SWCNT 'vine' while the larger ones facilitate the growth of the MWCNT 'tree' simultaneously.' Consequently, VT-CNTs composed of SWCNT 'vine' wrapping around MWCNT 'tree' can be self-assembled during the in-situ CVD of hydrocarbons.

"The self-assembly of the vine-tree-like structure can be ascribed to their tendency to minimize the interfacial adhesion energy between SWCNTs and MWCNTs." first-author Meng-Qiang Zhao explained to Phys.Org, "Typically, the SWCNTs formed on tiny catalyst NPs always grow much faster that the MWCNTs grown on large metal NPs. However, the VT-CNT structure herein can lead to the matching of the growth rate of SWCNT 'vine' and MWCNT 'tree'." The as-obtained VT-CNTs show a high specific surface area of ~650 $m^2 g^{-1}$ and a total pore volume of ~1.6 $cm^3 g^{-1}$.

CNTs are considered to be one of the most promising cathode materials for Li-S batteries because of their remarkable electrical conductivity and excellent mechanical properties. However, the low specific surface area ($^2 g^{-1}$) of MWCNTs limits their capability to accommodate sulfur at high loading amount and poor cycling stability for the MWCNT/S cathodes. Meanwhile, the SWCNTs are usually entangled with each other, which degrades their ability in the construction of efficient conducting networks. 'The VT-CNTs are expected to be promising candidate for high performance Li-S cathode materials.' explained Qiang Zhang, '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. The tree-like MWCNTs in VT-CNTs rendered robust electron pathways to ensure a good rate performance.'

A high capacity of 1418 mAh g^{-1} per sulfur can be achieved on the VT-CNT/S cathodes. A capacity of 530 mAh g^{-1} can still be retained even after 450 cycles at a current density of 1.0 C, with its initial capacity as 832 mAh g^{-1}. A cyclic fading rate of ca. 0.08 %/cyc was achieved. 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.

In the future, the researchers hope to precisely control the fine structure of VT-CNTs and achieve their large scale production, as well as further explore their applications in the areas of catalysis, environmental protection, nanocomposites, and electronic devices. 'The concept of vine-tree-like nanostructures is not limited to CNTs.' said Prof. Zhang, 'The fabrication of vine-tree-like nanostructures using other one-dimensional building blocks is foreseen, towards advanced materials with outstanding properties and performances."

More information: Zhao MQ, Peng HJ, Tian GL, Zhang Q, Huang JQ, Cheng XB, Tang C, Wei F. "Hierarchical Vine-Tree-Like Carbon Nanotube Architectures: In-Situ CVD Self-Assembly and Their Use as Robust Scaffolds for Lithium-Sulfur Batteries." *Advanced Materials*, 2014, 26(41), 7051-7058. doi:10.1002/ adma.201402488.

Provided by Tsinghua University