MATERIALS SCIENCE

The road to chirality-specific growth of single-walled carbon nanotubes

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Moore's law has been declared to be eventually nearing its end after nearly five decades, with silicon being the main building block for all computing chips [1]. The main roadblock in the development of transistors is the occurrence of the tunneling effect when the devices become small enough. A possible solution is finding alternative materials to fabricate a 'millivolt switch', which is at least as fast as silicon counterparts and generates much less heat.

Single-walled carbon nanotubes (SWNTs) are regarded as one of the most promising candidates as building blocks in next-generation electronics [2]. The most advanced opportunities demand the ability to form perfectly aligned, horizontal arrays of SWNTs with controlled structure using the chemical vapor deposition (CVD) method.

At present, the growth efficiency and selectivity of SWNTs with specific chirality are mainly explored through catalyst design in the CVD process. Although the CVD method has been extensively studied, how to improve the selectivity of SWNTs is still a great challenge. The key factors include the exact symmetry matching between catalysts and SWNTs in thermodynamics, and the optimization of the growth condition according to the growth kinetics of different SWNTs. The cooperation of the two factors will open up new
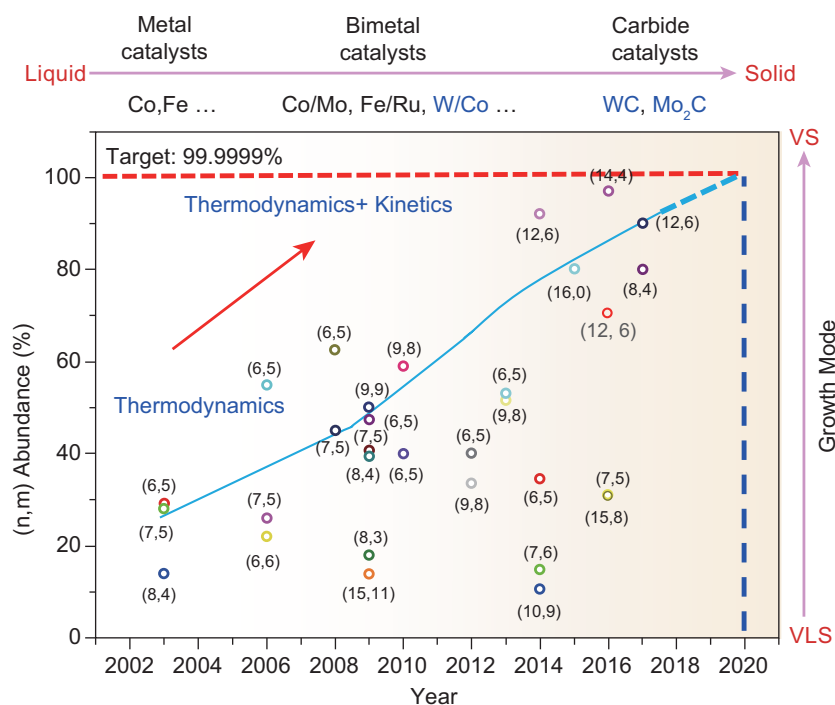
Figure 1. The development of selective SWNTs growth using different catalysts based on different growth modes. VLS and VS are the main mechanisms to explain the growth of SWNTs on different catalyst surfaces. Almost all the near-armchair tubes were enriched with a low selectivity in the power sample. The solid catalysts with extremely high melting points are marked in blue. The solid catalysts are beneficial for the chirality-specified growth of SWNTs based on the VS mechanism on the substrate surface. The vertical axis represents the reported abundance of SWNTs with specific chirality, and the target of the abundance before 2020 is marked by the red dashed line.

these solid catalysts, nucleation in thermodynamics of SWNTs on solid catalysts should be studied. We put forward the theory of symmetry matching between the edge of SWNTs and the face of solid catalysts. This not only can predict the chirality-specified growth of SWNTs through the symmetry of the catalysts, but also can provide guidance to design new catalysts to enrich the SWNTs with pre-defined chirality. Nevertheless, the symmetry matching is a simple model of bonding between catalysts and SWNTs, and needs much deeper investigation in both theory and experiments.

The growth of SWNTs, as a typical chemical reaction, is also affected by kinetics. In 2009, Feng Ding *et al.* suggested a screw-dislocation theory to explain the kinetics growth behavior of SWNTs, in which the growth rate is proportional to the Burgres vector of the dislocation that is related to the chiral angle [8]. They successfully explained the enrichment of near-armchair carbon nanotubes (see Fig. 1). However, this theory only considered liquid catalysts. The kinetic growth behavior should be further simulated on solid catalysts. This was done by Yakobson *et al.* in 2014 [9]. A slab model of solid catalyst was introduced to modify the Burgres vector of the dislocation, and they showed that $(2 m, m)$ tubes have the highest kinetic growth rate for the most dislocations [9]. Recently, our group proved it experimentally through controlling the concentration of carbon feeding to selectively poison catalyst nanoparticles, on which the tubes grow slowly. As a result, the tubes with smooth edges, such as the zigzag and armchair ones, are most difficult to enrich on solid catalysts, although (16, 0) and (6, 6) tubes have been reported to be prepared successfully. It can be noted that $(2 m, m)$ tubes could be enriched easily in addition to near-armchair tubes. A fact is that the enrichment of near-armchair tubes has been realized in the powder sample, but with low selectivity and, on the surface of substrate, $(2 m, m)$ tubes could be enriched with high selectivity (see Fig. 1). This may be due to the difference of catalysts in contact with

opportunities for the chirality-specific growth of SWNTs.

During the CVD growth of SWNTs, catalysts facilitate the decomposition of the carbon-feeding gases and serve as the nucleation centers of SWNTs [3]. The size and state of the catalyst affect the chirality of SWNTs from a thermodynamics point of view. Therefore, many researchers have tried to establish the exact relationship between SWNTs and catalysts from both theoretical calculations and experimental observations. However, the traditional metal catalysts, shown in Fig. 1 [4-7], showed relatively lower melting points, very different from the bulk melting point, and are termed as 'liquid catalysts'. A generally accepted vapor-liquid-solid (VLS) mechanism was put forward to explain the growth of SWNTs on these catalysts. However, it seems to be an extravagant hope that the chirality selectivity will be satisfactory, because the instability of catalysts

will lead to many possibilities during the growth of SWNTs. Nevertheless, efforts have been made to control the chirality of SWNTs by using solid-state catalysts through vapor-solid (VS) mechanisms instead of VLS mechanisms. In the periodic table of elements, tungsten and molybdenum are the metals with the highest melting points, but their catalytic activities are poor. Hence, rational design of new solid-state catalysts based on tungsten or molybdenum is required to improve catalytic activity. In 2014, Yan Li *et al.* first introduced Co to form the solid intermetallic W_6Co_7 catalyst with unique structure and high stability and obtained (12, 6) tubes with high selectivity, although the density was relatively low [5]. We designed carbides of tungsten and molybdenum as catalysts, which have higher melting points and improved catalytic activity, and grew (8, 4) and (12, 6) SWNT arrays with high density [6]. To further understand the role of

atmosphere when SWNTs are grown: for the latter, the catalyst was exposed to a homogeneous atmosphere and, for the former, a heterogeneous atmosphere was formed by diffusion in the holes of supports. Obviously, in a homogeneous atmosphere, kinetic controlling of SWNTs growth could be operated easily.

Considering the nucleation in thermodynamics and optimization of the kinetic growth environment, we enriched the (12, 6) tubes and (8, 4) tubes array using Mo_2C and tungsten carbide (WC) solid catalysts, respectively [6]. As shown in Fig. 1, the abundance of the enriched (12, 6) and (8, 4) tubes has a significant increase of up to 90% and 80%, respectively. However, for high-performance logic applications, the purity of single-chirality SWNTs should be higher than 99.9999% by the year 2020 [10]. Therefore, it is still an urgent task to improve the purity of the enriched SWNTs of single chirality on the substrate.

In summary, due to the well-known limits in various characterization methods, which make the current static not always satisfactory—for example, Raman is always resonant and transmission electron microscope (TEM) is usually very local—further efforts should be made and more exact characterization methods should be developed to yield enough discoveries in the controlled growth of SWNTs using the catalyst-mediated growth approach. It is expected that, in the near future, more single-chirality SWNTs will be synthesized with improved selectivity and growth efficiency by optimizing the thermodynamics during nucleation and the kinetics during the growth of SWNTs.

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