Although significant progress has been made in SWCNT synthesis, knowledge about the nucleation and/or growth mechanism, which could lead to type-selective growth and/or large scale production, is still very limited. Early on, it was believed that a very high temperature (e.g., 1000–2000 °C) was necessary for SWCNT synthesis, since arc discharge and laser ablation methods were mainly used. With the advent of now-popular CVD methods, this opinion is changing as the SWCNT growth temperature keeps getting lower, which is crucial for integrating SWCNT into hybrid electronics. Maruyama et al.1 reported SWCNT growth at 550 °C, Bae et al.2 reported it at 400 °C by using a plasma-enhanced CVD method, and recently Cantoro et al.3 further reduced it to 350 °C. Since the C–C bond is the strongest bond in nature, the surprisingly low growth temperature raises some compelling questions. What is the origin of the low threshold temperature or what dominates the growth of SWCNT at low temperature? Can one synthesize SWCNT at an even lower temperature, possibly even near room temperature? Theoretical analysis and models indicate that there are three relatively independent stages for the growth of a CNT on a catalyst: catalytic decomposition of carbon feedstock gas yielding C atoms, diffusion of these atoms to the tube end that is strongly attached to the catalyst surface, and incorporation of the C into the tube wall.4,5 Thermal activation is necessary for each of these stages, and thus, there must be a characteristic threshold temperature for each step. We define $T_{\text{dec}}$ as the lowest temperature sufficient to decompose the feedstock, $T_{\text{diff}}$ as the temperature above which C atoms can diffuse to the CNT end at reasonably high rate, and $T_{\text{g}}$ as the threshold temperature at which C atoms can readily be incorporated into the tube wall. Although the interplay of these stages can be complex, the highest threshold temperature of the three still must be the overall threshold temperature of the apparent CNT growth. Recent density functional calculations show that the diffusion barrier of a C atom on catalyst surface is only ~0.5 eV (e.g., diffusion barrier of C on Ni (111) surface6) so that $T_{\text{diff}}$ may be as low as room temperature. The feedstock decomposition sensitively depends on the type and size of the catalyst particle and the type of the chemical reaction, which is the feedstock itself. Finally, incorporation of C into CNT is feedstock independent, but knowledge about this stage is rather scarce. Thus, it remains difficult to see what is the dominant step determining the lowest growth temperature. We notice that, in most cases, the reported low temperature growth was achieved by using hydrocarbon sources with exothermic decomposition only (e.g., $\text{C}_2\text{H}_2 \rightarrow 2\text{C} + 2\text{H}_2, \Delta H^\circ = -38.2 \text{ kJ/mol}$ and $\text{C}_2\text{H}_4 \rightarrow 2\text{C} + 2\text{H}_2, \Delta H^\circ = -224.3 \text{ kJ/mol}$ at 800 °C)7 or with assistance of plasma. This seems to suggest that the decomposition of carbon feedstock limits CNT growth. If that is true, then the threshold of CNT growth with less active carbon feedstock, whose decomposition is endothermic, must be higher than that of using more active exothermic feedstock. In this paper, we report on the lowest temperature of SWCNT growth using endothermic decomposition of CH$_4$ gas. The observed lowest growth temperature (560 °C) is higher than what was previously reported for exothermic feedstock type. Our observation also indicates that the high decomposition threshold temperature of CH$_4$ limits SWCNT growth.

The Fe:Mo catalyst supported on Al$_2$O$_3$ powder (molar ratio Fe/Mo/Al$_2$O$_3$ of 1:0.2:1.5) used was prepared by an impregnation method.8 The catalyst reducibility was studied by temperature programmed reduction (TPR) in a Micromeritics Autochem 2910 under 10% H$_2$ in Ar (total gas flow 50 sccm). The growth of SWCNTs was performed by fast heating CVD using 50% CH$_4$ (Praxair, 99.999% purity) diluted in Ar (total gas flow 80 sccm). The catalyst was packed on a quartz capsule and positioned perpendicular to the gas flow, ensuring that all gas passes through it with complete accessibility. A mass spectrometer (MS), attached at the gas outlet of the reactor, monitored the catalyst activity in situ during the experiments by following H$_2$ formation (CH$_4$ → C + 2H$_2$, $\Delta H^\circ = +89.0 \text{ kJ/mol}$ at 800 °C). Prior to the synthesis, the catalyst was reduced under H$_2$/He gas mixture (40 sccm/100 sccm) for 15 min at temperatures between 500–900 °C. The carbonaceous samples obtained were characterized by Raman scattering and transmission electron microscopy (TEM).

The TPR curve for the Fe:Mo:Al$_2$O$_3$ catalyst (Figure 1a) shows several reduction peaks. The features observed below 500 °C are similar to those observed for monometallic Fe oxide catalyst supported on alumina, which have been related to the three phases of reduction of iron oxide in the form of hematite to metallic Fe (transformation of Fe$_2$O$_3$ → Fe$_3$O$_4$ → FeO → Fe).9 The high temperature peak (~830 °C), which could be related to residual oxygen in the smaller metal particles10 and the effect of Mo, shows that the common reduction procedure11,12 at ~500 °C under a flow of He/H$_2$ is not enough to completely reduce the metal catalyst in...
The presence of a significant amount of residual oxygen in the catalyst after common low temperature reduction (∼500 °C) may have a huge impact on the SWCNT growth. In fact, it was demonstrated for Fe that the inactivity of the oxide catalyst for growing SWCNTs at ∼680 °C could be reversed after a reduction at 500 °C for long periods of time (10−20 h). Moreover, it has been shown that metals like Cu, Au, Pd, or Pt, which initially were considered not active for nanotube growth, can indeed nucleate SWCNTs after a reduction at ∼850 °C.\textsuperscript{11} To investigate the effect of the reduction temperature on the SWCNT synthesis, we first studied its effect on the catalytic activity. Figure 2a shows the dependence of the catalyst activity for CH\textsubscript{4} decomposition as a function of the reaction temperature with and without reduction. Here, no difference is observed between the curves of the unreduced and reduced catalysts at 500 °C for 60 min, which is in agreement with previously reported results for a similar catalyst.\textsuperscript{8} However, the vigorously reduced catalyst (at 900 °C for 15 min) shows a downshift of ∼150 °C in the onset temperature for decomposition of the hydrocarbon gas, which points to a decrease in the activation energy for decomposition of CH\textsubscript{4}. Further increasing of the reduction temperature (∼970 °C) did not bring this temperature down more. The result shows that indeed the degree of reduction of the sample greatly affects the catalyst’s ability to decompose CH\textsubscript{4}. This decrease in temperature at which CH\textsubscript{4} decomposition starts allowed us to grow SWCNTs as low as 560 °C. The Raman radial breathing modes show a relatively broad diameter distribution (0.7−2 nm) of grown SWCNTs (Figure 2b). The ratio of G and D-bands intensities is low, as the graphitization level of the sample is expected to be poor due to the low synthesis temperature. To our knowledge, this is the lowest reported temperature for growth of SWCNTs with this catalyst composition and CH\textsubscript{4} via thermal CVD. Previously reported minimum temperatures with Fe/Mo catalyst were around 680 °C,\textsuperscript{8,16} where the catalyst was unreduced or submitted to a traditional reduction pretreatment at 500 °C (10% H\textsubscript{2} in He for 10−20 h). A SWCNT growth temperature of ∼600 °C was reported with CH\textsubscript{4} but using a Ni catalyst,\textsuperscript{17} where a H\textsubscript{2} treatment at 650 °C is crucial to enable the growth at such low temperature. Therefore, whereas the use of oxidizing environments\textsuperscript{18,19} improves both SWCNT yield and quality, the presence of residual oxygen in the catalyst suppresses the low temperature growth.

The above analysis shows that under our experimental conditions, once carbon feedstock decomposition begins, the SWCNT grows instantly. Therefore, the low temperature growth is limited by the feedstock decomposition. As expected, the lowest growth temperature when using endothermic feedstock, CH\textsubscript{4}, is still significantly higher than that when using exothermic feedstock. It is also reasonable to suggest that the threshold temperature $T^*_g$ of incorporating C into the SWCNT wall must be lower than the recently reported lowest growth temperature.\textsuperscript{15} This is easy to understand because incorporating C to the tube wall is exothermic, although one should keep in mind that the defect healing involved in the formation of good quality SWCNT requires higher temperature. Indeed, as observed experimentally, SWCNTs of rather low quality often emerge at reduced temperatures.

Our study also suggests that, by using more active carbon feedstock or somehow facilitating its decomposition (e.g., with assistance of plasma), one could enable the synthesis of SWCNT at an even lower temperature, for example, $T \approx 300$ °C. At least the low levels of $T_{diff}$ and $T_g$ make the effort in this direction more promising. One more encouraging fact is that multiwall CNTs can be synthesized at much lower temperature (e.g., 175 °C with CCl\textsubscript{4} as feedstock),\textsuperscript{20} which our approach may decrease even more. Experiments involving the synthesis of SWCNT at an even lower temperature are in progress.

References

(19) Wen, Q.; Qian, W.; Wei, F.; Ning, G. Nanotechnology 2007, 18, 215610.