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Revolution in Carbon Nanotube Synthesis –"Super Growth"

Don N. Futaba[1,2], Kenji Hata[2], Kohei Mizuno[2], Takeo Yamada[2], Tatsunori Namai[2], Yuhei Hayamizu[2], Motoo Yumura[2] and Sumio Iijima[2]

[1]Japan Fine Ceramics Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan

[2]Research Center for Advanced Carbon Materials, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan

1. Introduction -"Super-Growth"

We present "Super-Growth" where the introduction of a small and controlled amount of water into the growth ambient of standard CVD enhanced the activity and the lifetime of the catalysts [1]. From this water-stimulated catalytic activity dense, impurity-free, and vertically aligned single-walled carbon nanotube (SWNT) forests with millimeter-scale heights were grown and patterned into scaled-up macroscopic organized structures with defined shape, providing nanotube material with carbon purity above 99.98%. These remarkable features make the super-growth CVD quite unique from existing SWNT synthesis methods. The water-assisted synthesis method addresses many critical problems that currently plague carbon nanotube synthesis.

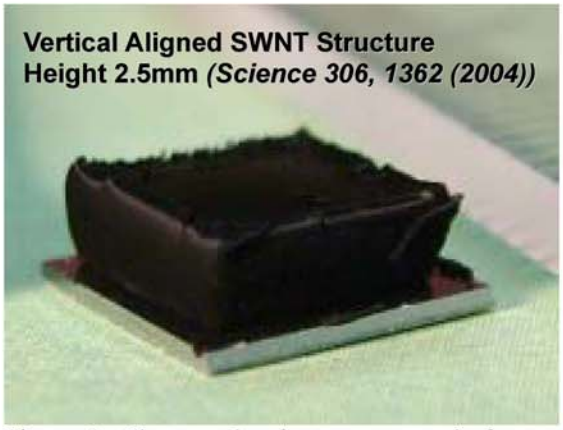

Figure 1: Photograph of a super-growth forest grown in a 10 minute growth time standing 2.5 mm in height.

2. Characterization - 84% Catalyst Activity

We propose a statistical and macroscopic analysis to estimate the catalyst activity of water-assisted growth (super-growth) of SWNTs and to characterize SWNT forests. The catalyst activity was estimated to be 84% (±6 %), the highest ever reported, highlighting the high efficiency of super-growth. Accurate quantification of the catalyst activity required accurate determination of the SWNT area density and the catalyst area density. Given the tangible amounts of tubes produced by a typical growth, a macroscopically statistical approach was necessary for this evaluation. SWNT forests were characterized to have 0.037 (±0.002) g/cm^3 mass density, 3.0 (±0.07) nm average SWNT diameter, 5.2 x10^{11} (±0.35 x10^{11}) tubes/cm^2 SWNT area density, and 6.2x10^{11} (±0.26 x10^{11}) catalysts/cm^2 catalyst area density. The SWNT forest was found to be a very sparse material where SWNTs represent only 3.6% of the total volume. This structural sparseness is believed to play a critical role in achieving highly efficient growth.

Growth with high catalyst activity has immediate benefits not only for the mass production of SWNTs, but more importantly the SWNT material would contain much less catalytic impurities thus enabling the immediate use of as-grown material without any purification. We wish to emphasize that the analysis of catalyst activity of 84% was implemented on an arbitrary sample, and no growth optimization had been carried out to maximize the catalyst activity. Therefore, we are confident that further improvements are possible by additional tuning of the super-growth to achieve catalyst activities close to 100%, one of the ultimate goals of SWNT synthesis. If 100% catalyst activity is achieved, significant breakthroughs could be realized in various fields, e.g., it might be provide a solution for reliable assembly of CNT field effect devices, opening up an exciting opportunity to realize integrated carbon nanotubes circuits. Considering the high catalyst activity of 84%, we envision that the emergence of super-growth CVD represents the end of the era where low catalyst activity had been one of the serious issues in

SWNT synthesis.

3. Growth Kinetics

We were further motivated to cultivate a general understanding of the kinetics of this new and promising synthetic method. Knowledge of the kinetics is critically important to understand the mechanism of the super-growth CVD and to the mechanism of the super-growth CVD and to further improve SWNT synthesis to new levels. We have addressed this important issue by formulating a numerical growth model that describes the time-evolution of the super-growth [2]. This growth model served as the key point to quantitatively analyze the kinetics of the super-growth and to gain insight into the effect of water. Moreover, our growth model and subsequent analysis served as a guide in optimizing the growth conditions; a matter of significant importance for super-growth CVD because the use of water adds an additional dimension of complexity.

As revealed by a time-evolution analysis, the growth rate was highest at the onset of growth, then gradually decreased with time over 20 minutes, and finally terminated at a height of 970 μm (Fig. 2). Similar behavior with varying lifetimes and terminal heights was observed on a number of time-evolution experiments that covered a wide range of growth conditions. We developed a simple growth model of the form $H(t) = \beta\tau_o\left(1 - e^{-t/\tau_o}\right)$. This means that growth can be described by two physically meaningful fitting parameters: β is the initial growth rate (IGR) and τ_o is the characteristic catalyst lifetime. Fitting our growth-equation to the experimental time-evolution data yielded excellent agreement ($R^2 = 0.9940$), supporting the soundness of our modeling.

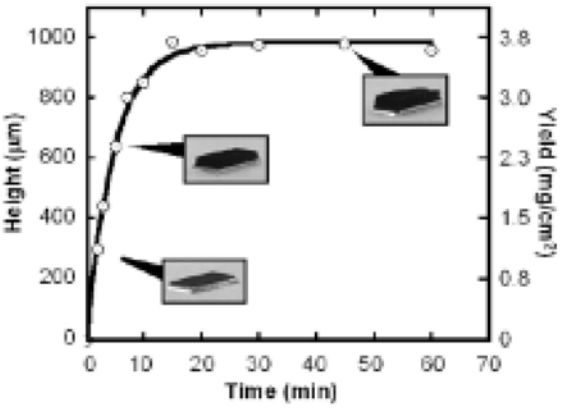

Fig. 2. SWNT forest height as a function of the growth time. The solid line indicates the curve fit to the growth equation. Inset photographs show the samples at various stages of growth.

Further analysis revealed that a scaling relation between ethylene and water and that the balance of the ethylene and water is the most critical factor for the super-growth. By this we mean that the same maximum height can be achieved by both a slow growth with a long lifetime and a fast growth with a short lifetime given that the water/ethylene ratio is the same. Furthermore, the existence of this scaling law suggests that the catalysts consume a specific number of ethylene and water molecules before they die, and this specific number is determined by the water/ethylene ratio. Moreover, it implies that each growth event in which a carbon atom is supplied from the gas phase and incorporated into a catalyst, and solidified as a SWNT can be considered as a Markov process, i.e., growth events are independent. This implies that the rate limiting process of the SWNT growth in this growth parameters window is the supply of carbon to catalysts from the gas phase.

4. Acknowledgements

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[2] D.N. Futaba, K. Hata, T. Yamada, K. Mizuno, M. Yumura and S. Iijima, Physical Review Letters (*in press*).