CVD Growth of Single-Walled Carbon Nanotubes

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CVD growth of single-walled carbon nanotubes (SWNTs) will be discussed with recent alcohol CVD experiments incorporating nitrogen, molecular dynamics simulations, and FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectroscopy.

Metal nanoparticles are believed to the essential catalyst for CVD growth of SWNTs for decades. Even though there are a few exceptions such as growth from fullerenes and cloning growth, efficient CVD growth always utilized metal nanoparticles. A nanoscale metal catalyst such as Fe, Co, Ni and Cu are used for practical CVD growth. Depending on carbon source and reaction environments, one of these metal is preferred: Fe is preferred for CH_4+H_2 CVD and CO disproportional CVD; Co is preferred for Ethanol CVD. Bimetallic catalysts such as Co/Mo and Co/Cu are often used, and Al_2O_3 support layer can be often preferred than SiO_2. Most of CVD conditions are intuitively determined by experiments, because the structure and chemical composition of nanoparticles during CVD growth is still not clear. For further growth control of diameter of SWNT and chirality or selective growth of metallic and semiconductor, detailed understanding of the dynamics process of catalyst and SWNT growth is essential.

The chemical environment is quite important for CVD growth. We synthesized SWNTs with small diameter and narrow diameter distribution using acetonitrile (AcN)-mixed ethanol (EtOH) feedstock. Due to the presence of nitrogen (N) during synthesis, the SWNT mean diameter was dramatically reduced from approximately 2.1 nm to less than 1 nm as AcN was added as carbon source [1, 2]. Surprisingly, the main nitrogen configuration was found to be encapsulated diatomic N_2 molecules interior of SWNTs with the content of 1 at % [3]. As the sequence of feedstock was switched during synthesis, SWNT diameter was changed along the vertically aligned array. A majority of nanotube junctions between two different diameter nanotubes were found to be discontinuous, while a minority of continuous junctions were revealed by high-resolution TEM [4]. This diameter modulation was reversible upon the sequence of feedstock introduction.

We also address the role of nitrogen on influencing the SWNT diameter in which nitrogen affects only the surface of the catalyst particle, resulting in a change from the Octopus to the VLS growth mode predicted by molecular dynamics simulations. By using ^{15}N isotope of acetonitrile, the catalytic decomposition of acetonitrile in the initial reaction step can be studied [5]. On the other hand, the initial decomposition process of acetonitrile on metal clusters is directly measured by using FT-ICR mass spectrometer.

References

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