

III-G Structure and Properties of Carbon Nanotubes and Nanohorns

We studied growth of single-wall carbon nanotubes (SWNTs) and single-wall carbon nanohorns (SWNHs), and enabled their high-yield and structure-controlled growth. It is shown that the nanometer-scale tubule structures caused the unique behaviors such as one-dimensional fullerenes-crystal growth inside SWNTs, size-selective adsorption of gas molecules inside SWNHs, and selective adsorption of polypeptides by the oxidized SWNHs. In some application of SWNTs and SWNHs, their immobilization on Si wafers was necessary, which was made possible by using bi-functional molecules with amine at one end and silane at the other end of the linear hydrocarbon molecules. We developed structure analyses methods of carbon nanotubes with electron diffraction analyses with transmission electron microscopy and Raman spectroscopy, and found there is no correlation between the symmetries of inner and outer tubes of double-wall carbon nanotubes.

III-G-1 Causes of Different Catalytic Activities of Metals in Formation of Single-Wall Carbon Nanotubes

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When single-wall carbon nanotubes (SWNTs) were formed by pulsed Nd:YAG laser ablation or arc discharge, the yield depended on the metal catalyst: NiCo > Ni ~ NiFe » Co ~ Fe > Pd ~ Pt. It appears that an effective catalyst for SWNT growth must satisfy three conditions: it must be a good graphitization catalyst, have low solubility in carbon, and have a stable crystallographic orientation on graphite. NiCo, Ni, and NiFe satisfy these three conditions. The poor catalytic activities of Co, Fe, Pd, and Pt for SWNT formation would be explained by the ineffectiveness of Pt and Pd as graphitization catalysts, crystallographic orientation instability of Co crystals on graphite, and high solubility of Fe in graphite.

III-G-2 Selective Production of Single-Wall Carbon Nanohorn Aggregates and Their Formation Mechanism

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Single-wall carbon nanohorn (SWNH) aggregates can be produced by CO₂ laser vaporization of carbon, and a single aggregate can take either a “dahlia-like” or “bud-like” form. We found that “dahlia-like” SWNH aggregates were produced with a yield of 95% when Ar at 760 Torr was used as the buffer gas, while “bud-like” SWNH aggregates were formed with a yield of 70 or 80% when either He or N₂ at 760 Torr was used. The internal structures of both aggregates were studied by partially burning them in an O₂ atmosphere. We were

then able to examine the mechanism for the formation of SWNH aggregates.

III-G-3 Fullerene Formation via Pyrolysis of Ragged Single-Wall Carbon Nanotubes

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A new path of fullerene formation via pyrolysis of ragged single-wall carbon nanotubes (r-SWNTs) which were treated by ultrasonication with an organic solvent followed by heating in oxygen gas is reported. Mass spectrum and high-performance liquid chromatography results indicated that C₆₀, C₇₀, and higher fullerenes existed in products obtained through the pyrolysis of the r-SWNTs at above 800 °C in vacuum. We suggest that the pyrolysis of r-SWNTs originates from holes and defects in the r-SWNTs.

III-G-4 Diameter-Selective Resonant Raman Scattering in Double-Wall Carbon Nanotubes

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[*Phys. Rev. B* **66**, 075416 (8 pages) (2002)]

Double-wall carbon nanotubes (DWNT's) have been studied by Raman scattering using different excitation wavelengths and their spectra compared to those of single wall nanotubes (SWNT's) and C₆₀-SWNT peapods. Raman scattering from the radial and tangential vibrational modes of very small diameter $d \sim 0.6\text{--}0.9$ nm secondary (interior) semiconducting tubes within the DWNT can be unambiguously identified with 647.1 and 1064 nm excitations. The frequency of the tangential displacement vibrational modes identified with these secondary (interior) tubes is found to be downshifted by ~ 7 cm⁻¹ relative to that of the larger primary (exterior) tubes that exhibit a diameter $d \sim 1.3\text{--}1.6$ nm. This downshift strongly suggests that at

small tube diameters (*i.e.*, $d \sim 0.7$ nm), the associated wall curvature of the nanotube may require an admixture of sp^3 character in the C–C interaction. Our results also show that the value $\gamma_0 = 2.90$ eV for the nearest C–C tight binding integral is consistent with the resonant enhanced Raman scattering from DWNT's.

III-G-5 Linking Chiral Indices and Transport Properties of Double-Walled Carbon Nanotubes

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[*Phys. Rev. Lett.* **89**, 155501 (4 pages) (2002)]

We performed *in situ* transport measurement in a transmission-electron microscope (TEM) on individual double-walled carbon nanotubes (DWNT). Using selected-area electron diffraction, the chiral indices of the two tubes constituting the DWNTs were determined through careful comparison with theory. We discuss the case of a DWNT whose two tubes have a gap at half filling and show a finite density of delocalized state at the Fermi level. The exact determination of chiral indices should be reachable in any transport-measurement experiment with samples that allow TEM characterization.

III-G-6 Diameter-Selective Removal of Single-Wall Carbon Nanotubes through Light-Assisted Oxidation

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[*Chem. Phys. Lett.* **374**, 132–136 (2003)]

When single-wall carbon nanotubes (SWNTs) were treated with H₂O₂, rates of SWNT oxidative-degradation were found to be enhanced with irradiation of light. Raman spectroscopic study indicated that, when the irradiation periods were 2 and 5 min, the radial breathing modes of SWNTs having gap energies corresponding to the wavelength of the irradiated light selectively disappeared. This result suggests that SWNTs having a gap energy corresponding to the wavelength of the irradiated light were preferentially removed.

III-G-7 Single-Wall Nanostructured Carbon for Methane Storage

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[*J. Phys. Chem. B* **107**, 4681–4684 (2003)]

Open single-wall carbon nanohorns (SWNHs) were

compressed repeatedly at 50 MPa to generate a nanocarbon material of high bulk density. TEM observations and Raman spectroscopy revealed a significant distortion in the structure of the compressed SWNHs. The obtained nanostructured disordered carbon exhibits a high methane storage capacity, reaching 160 cm³/cm³ of nanocarbon at 3.5 MPa and 303 K. Comparison of the experimental results with grand canonical Monte Carlo simulations indicates the importance of the adsorption in the interstitial channels for the high total adsorption capacity of the generated nanostructured carbon.

III-G-8 Nanowindow-Induced Molecular Sieving Effect in a Single-Wall Carbon Nanohorn

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Subnanoscale windows (nanowindows) were donated to the walls of single-wall carbon nanohorns (SWNHs) by oxidation in oxygen at different temperatures of 573–693 K. We determined the accessibility of internal nanospaces of the SWNHs through nanowindows to He, Ar, N₂, CH₄, SF₆, and C₆₀. An explicit molecular sieving effect of SWNHs due to the nanowindow was shown.

III-G-9 Binary Nano-Materials Based on Nano-Carbons: A Case for Probing Carbon Nanohorns' Biorecognition Properties

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A critical step toward the construction of complex architectures based on nanoscale carbonaceous materials is to interface these structures with other useful nanoscale building blocks. Herein we report the synthesis of a new class of binary nanomaterials from single-walled carbon nanohorns and nanoparticles by utilizing a bifunctional molecule as the bridging interconnect. Characterization of the materials by transmission electron microscopy, energy-dispersive X-ray spectroscopy, Raman spectroscopy, and thermogravimetric analysis unambiguously proves the formation of binary nanostructures. The strategy reported here is expected to be generic and readily applicable to carbon nanohorns' interfacing with other nanoscale materials, such as Pt, in the construction of fuel cells. Significantly, with these binary nanomaterials, distinct differences in peptide recognition properties have been identified for carbon nanohorns treated under different conditions through a phage-display enzyme-linked immunosorbent assay. Those peptide recognition motifs are important for exploiting this class of materials in

bioassembly, bioseparation, and biosensing applications.

III-G-10 A Surface Modification Approach to the Patterned Assembly of Single-Walled Carbon Nanomaterials

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A surface modification strategy has been employed for the patterned assembly of single-walled carbon nano-materials onto oxide surfaces. The method relies on distinct molecular recognition properties of different functional groups toward the carbon graphitic structure. The surface modification starts with reactions between bifunctional molecules **1** (with amino and silane groups) and hydroxyl groups on an oxide substrate, generating an amine-covered surface. This is followed by a coupling step where bifunctional molecules **2** (with succinimidyl ester and pyrene groups) react with amines. With one area covered with pyrenyl groups and the other one with hydroxyl groups, patterned assembly of a single layer of single-walled carbon nanohorns (SWNHs) has been demonstrated. The strategy employed, herein, is quite generic and applicable to a variety of oxide substrates, including quartz, SiO₂ layer on Si, and Indium Tin oxide (ITO). Since silane chemistry is compatible with soft or lift-off lithography, an extension of this methodology to micrometer scale patterning has been achieved and a further reduction of the size feature should be possible. In addition, patterned assembly of single-walled carbon nanotubes (SWNTs) has also been realized. These surface immobilized structures should open up new possibilities in such areas as nano-electronics, chemical sensing, field emission displays, nano-tribology, and cell adhesion/bio-recognition investigations.