

Templating Effect of Hydrogen-Passivated Silicon Nanowires in the Production of Hydrocarbon Nanotubes and Nanoonions via Sonochemical Reactions with Common Organic Solvents under Ambient Conditions

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The discovery of buckminsterfullerene (C₆₀)¹ led to extensive series of fullerenes, multi/single-wall nanotubes,^{2,3} and nanoonions.⁴ The unique electronic, optical, and mechanical properties of these nanomaterials make them topics of intensive investigations. Nowadays, carbon nanotubes (CNTs) and nanoonions (CNOs) can be produced by such diverse techniques as arc discharge,² laser ablation,⁵ chemical vapor deposition (CVD),⁶ electron beam irradiation and high-temperature annealing,^{4,7} etc. Until now, however, these carbon nanostructures can only be produced under such severe conditions as high temperature, high vacuum, high voltage arc discharge, or high-energy electron irradiation. Many of these preparative methods require specialized equipments such as lasers and CVD or metal catalysts. A recent report of the synthesis of CNTs⁸ and CNOs⁹ by arc discharge using graphite electrodes in water at room temperature prompted us to report herein a simple sonochemical solution method using silicon nanowires (SiNWs) as templates to produce carbon nanostructures under ambient conditions (room temperature and atmospheric pressure) and without metal catalysts.

The SiNWs are one-dimensional wires of silicon, which can be synthesized by thermal evaporation of SiO₂¹⁰ or by laser ablation of metal-containing silicon targets.¹¹ The SiNWs were prepared by the thermal evaporation method.¹⁰ The outer oxide layer can be removed by a controlled HF treatment. The surfaces of the HF-etched, oxide-free SiNWs have been found to be passivated by hydrogen (i.e., SiH_x species, where $x = 1-3$) and exhibit moderately high reactivity in solution.¹² In our attempt to disperse oxide-free SiNWs in common organic solvents, we discovered a new type of well-structured, hydrocarbon nanomaterial which may be termed hydrocarbon nanotubes (HCNTs) and onions (HCNOs), which is the subject of this communication.

The new HCNTs and HCNOs can be produced by dispersing HF-etched SiNWs in certain common solvents such as CHCl₃, CH₂Cl₂, CH₃I, etc., followed by bath sonication for 15 min under ambient conditions. The yellowish solution turned turbid within minutes of sonication and exhibited a Tyndal effect characteristic of colloidal solutions. The products were characterized by high-resolution transmission electron microscopy (HRTEM, Philips CM200 FEG, operated at 200 keV), electron energy loss spectroscopy (EELS), which was attached to HRTEM, and Raman spectroscopy using a Renishaw micro-Raman spectrometer at room temperature.

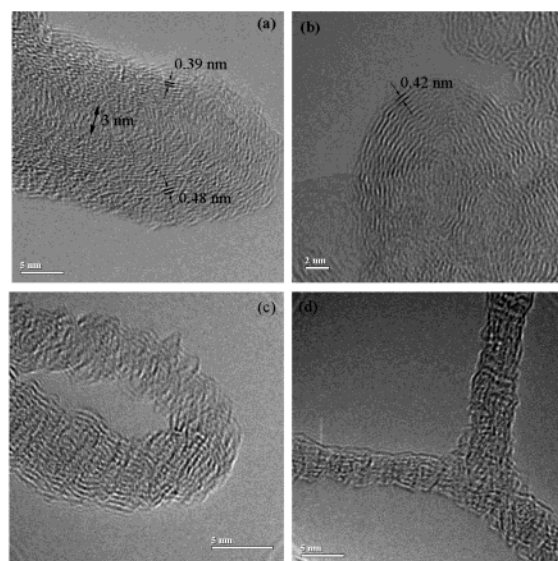


Figure 1. HRTEM images of a new type of hydrocarbon nanomaterial: (a) nanotube (inner and outer diameters of 3 and 18 nm, respectively), (b) nano onion, (c) loop, and (d) Y-shape carbon nanostructures with interlayer spacing larger than 3.4 Å.

In addition to the commonly observed CNTs and CNOs with interlayer spacing of 3.4 Å, a new type of hydrocarbon (HC) nanostructure, with interlayer spacing varying from 3.5 to 5.8 Å, was observed. These nanostructures exhibit many shapes and forms, the most common ones being multiwall hydrocarbon nanotubes (HCNTs) and onions (HCNOs) as depicted in Figure 1a and b, respectively. Other shapes such as faceted polyhedral onions, twisted tubes or loops (Figure 1c), Y-shape (Figure 1d), or other networks can also be found. These carbon nanostructures are different from conventional CNTs and CNOs in that they all have rough, wavy layers and are easily shrunk, collapsed, or damaged by the electron beam under TEM. Nonetheless, these HCNTs/HCNOs exhibit well-structured morphologies and can be converted to the conventional CNTs/CNOs (with interlayer spacings of 3.4 Å) upon prolonged sonication.

We believe the SiNWs serve as templates for the formation of these nanostructures, as evidenced by the “caught-in-the-act” TEM picture shown in Figure 2a. Here, a HCNT of about 4 nm in diameter and 65 nm in length was found to connect the tip of one SiNW (A) to the body of another SiNW (B). The SiNWs have diameters of about 30 nm. The EELS results, taken from the area between “A” and “B”, reveal that it is comprised purely of carbon.

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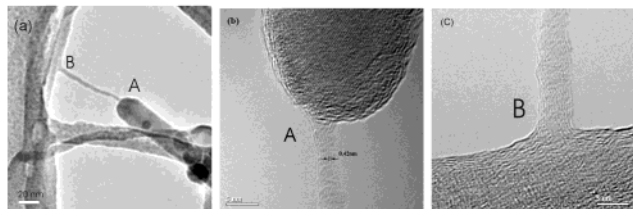


Figure 2. (a) TEM image of a HCNT connecting the tip of a SiNW (A) to the body of another SiNW (B). (b) HRTEM image taken from area "A" in (a). (c) HRTEM image taken from area "B" in (a).

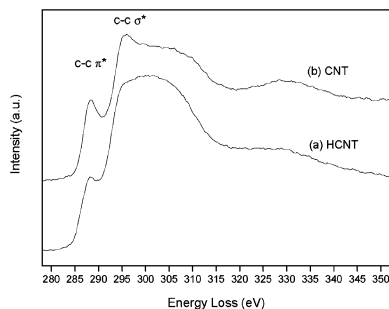


Figure 3. The single-tube EELS results of the new HCNT (curve a) and the conventional CNT (curve b). Both were found in the same sample.

The HRTEM image in Figure 2b, taken from area "A" in Figure 2a, showed that this new type of HCNT has an interlayer spacing of 4.2 Å, emanating from the tip of SiNW "A". This seven-layered HCNT (or a total of 14 layers) is connected to SiNW B as shown in Figure 2c, taken from area "B" in Figure 2a. In some cases, there are a few layers of amorphous carbon between the SiNW surface and the hydrocarbon nanotubes as is evident in Figure 2c. TEM element mapping results (not shown) confirmed the chemical compositions of the SiNW (the template) and the HCNT (the product).

While further work is needed to fully understand the mechanism of the formation of these HCNTs on SiNWs, we believe that the new carbon structures are associated with active reaction sites on the surfaces of the SiNWs. In this respect, when the as-synthesized SiNWs (sheathed with an oxide layer) were immersed in CHCl_3 and treated by bath sonication in the same way, no carbon nanostructures were found. This result confirmed that the carbon nanostructures arose from the reactions between the $-\text{SiH}_x$ ($x = 1, 2, 3$) species on the surfaces of the SiNWs and the solvent molecules. These findings provide a clue to the mechanism of formation of the HCNT(O)s/CNT(O)s. On the surfaces of the SiNWs, the organic solvent molecules react with the SiH_x moieties and, under the local heating condition of the sonication process, result in the elimination of the substituents of the solvent molecules. In the case of CHCl_3 , the reaction between the Si-H and C-Cl bonds results in dehydrochlorination, giving rise to CH units which polymerize to form the hydrogenated graphite sheets¹³ that wrap around the SiNWs (templating effect). Further sonication causes the SiNWs to shed off the HCNTs, refreshing the SiNW surfaces for further reaction. The extruded HCNTs or HCNOs usually collapse to form solid or hollow tubes or onions of smaller diameters (see Figure 1). A solid HCNT extruded from a SiNW is depicted in Figure 2a. Finally, these hydrocarbon nanostructures may ultimately transform (sometimes partially) to the conventional CNTs and CNOs with interlayer spacings of 3.4 Å upon prolonged sonication, resulting in hybrid HCNT(O)s/CNT(O)s and, ultimately, CNT(O)s.

We believe that these new structures of HCNTs/HCNOs are formed by networks of a chair-form cyclohexane-like hexagonal structure, similar to that of partially hydrogenated graphite on the

one extreme and that of the amorphous hydrocarbon (a-C:H) on the other. Morphologically, they are similar to the conventional CNTs or CNOs except that C-H bonds have been inserted between layers, thereby converting curved sp^2 sheets into puckered sp^3 layers or combinations thereof. The more C-H bonds being inserted, the larger will be the interlayer spacing. The interlayer spacing also depends on the degree of packing between adjacent layers. The single-tube EELS of a hydrocarbon nanotube (HCNT) is compared with that of a conventional carbon nanotube (CNT) in Figure 3. The main difference between the new HCNT and the conventional CNT is that HCNT exhibits less sp^2 bonds and more disordered sp^3 bonds than does CNT, as evidenced by the fact that the edge ratio sp^3 (C-C)/ sp^2 (C=C) is approximately 1 for the conventional CNT but 1.5 for the new HCNT.

The Raman spectra of the products further confirmed that the carbon structures are the reaction products of SiNWs and the solvent molecules. The intense peaks at 517 and 960 cm^{-1} can be ascribed to the scattering of the first-order optical phonon and the overtone of TO (L) of Si in SiNWs, respectively. More importantly, there were three weak peaks at 1300, 1450, and 1600 cm^{-1} . The peaks at 1300 and 1450 cm^{-1} can be assigned to sp^3 (C-C), whereas that at 1600 cm^{-1} can be assigned to sp^2 (C=C) stretching frequencies of the HCNT(O)s. These bands are very different from that of normal CNTs which has a strong band at 1580 cm^{-1} (sp^2) and a weaker band at 1348 cm^{-1} (sp^3).

In summary, a new type of hydrocarbon nanotubes and onions, with interlayer spacings ranging from 3.4 to 5.8 Å, was discovered by reacting SiNWs with common organic solvents in a laboratory sonicator under ambient conditions (room temperature and atmospheric pressure). We believe that sonication not only promotes the reaction between SiH_x and the organic molecules but also facilitates the formation of the different types/shapes of carbon nanostructures as well as causes the extrusion (or demolding) of the products. Work is in progress to discern the reaction pathway(s) and/or mechanism.

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