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A novel nanostructure of nickel nanotubes encapsulated in carbon nanotubes

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A novel nanostructure of Ni nanotubes encapsulated in carbon nanotubes has been obtained *via* the pyrolysis of C_2H_2 on an array of Ni nanotubes in an alumina membrane support and a possible mechanism has been proposed.

Since the discovery of carbon nanotubes (CNTs) in 1991,[1] a great amount of research work on CNTs and related nanostructures has been carried out due to their extraordinary mechanical and electronic properties and potential applications such as use in electron field emitters in panel displays, single-molecular transistors, scanning probe microscope tips, gas and electrochemical energy storage, *etc*.[2–8] Catalytic hydrocarbon decomposition, laser ablation and arc-discharge evaporation of graphite are often used to obtain various carbon nanotubular structures, such as straight, curved, planar-sprial and helical shapes,[9] and in some cases, metal nanoparticle- or nanowire-filled carbon nanotubes can also be obtained.[10–12] Using different catalysts, the CNTs produced have different intrinsic structures, implying different carbon growth mechanisms. Study on CNT production using different catalysts is therefore important for fundamental and technological interest. In this communication, we report an interesting result concerning the formation of a novel nanostructure of tubes within tubes *via* pyrolysis of C_2H_2 on an array of Ni nanotubes.

An array of Ni nanotubes was fabricated in the pores of an alumina membrane (Whatman, quoted pore diameter 100 nm) following our previous method.[13] Then, the array of Ni nanotubes with alumina membrane support lying on a ceramic plate was placed in a horizontal quartz reactor and heated to 600 °C under flowing gas containing 5% H_2 and 95% Ar for 1 h. The temperature of the furnace was then increased to 650 °C, and the source gas containing 10% C_2H_2, 5% H_2 and 85% Ar was passed through the reactor at a flow rate of 50 mL min^{-1} for 1 h. Then the source gas stream was switched to a flow of 5% H_2 and 95% Ar and the furnace was cooled to room temperature gradually. The sample, after removing the alumina using 2 mol L^{-1} NaOH, was collected on a carbon-coated copper grid for observation of the microstructures with a transmission electron microscope (TEM, JEM-200CX). Energy dispersive spectroscopy (EDS) was performed using a transmission electron microscope with an Oxford Link ISIS microanalyzer. Phase characterization was performed by means of X-ray diffraction using a D/Max-RA diffractometer with Cu-Kα radiation.

Pyrolysis of C_2H_2 on the array of Ni nanotubes at 650 °C yields nanostructures as can be seen from the TEM images in Fig. 1 at different magnifications. Interestingly, the images clearly reveal novel nanostructures of tubes within tubes. An energy-dispersive spectrometry (EDS) analysis of the nanostructures has been performed. The results indicate that the nanostructures are composed of carbon and nickel, moreover, the outer wall is only carbon. Corresponding selected area electron diffraction of the sample (the inset picture in Fig. 1B) demonstrates that the nanostructures are polycrystalline because the bright spots are composed of small arcs along the circles. Further characterization comes from XRD (Fig. 2). The diffraction peaks in the range $25 < 2\theta < 80°$ can be indexed as fcc structure Ni(111) and (200) in good concordance with the ASTM standard 4-850, and graphitic C(002), though it is uncertain as yet if the (002) diffraction peak arises from carbon nanotubes or graphitic particles present in the sample. Other peaks in Fig. 2 can be indexed to chaoite carbon (203), (205) and (304), in good concordance with the ASTM standard

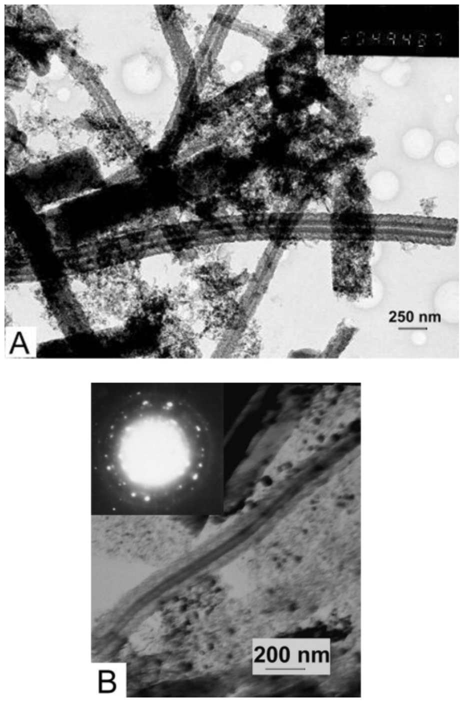

Fig. 1 (A) and (B): TEM images at different magnifications of a sample prepared by decomposition of C_2H_2 on an array of Ni nanotubes. The inset picture shows the corresponding selected area electron diffraction of the nanostructure of a tube-in-tube in (B).

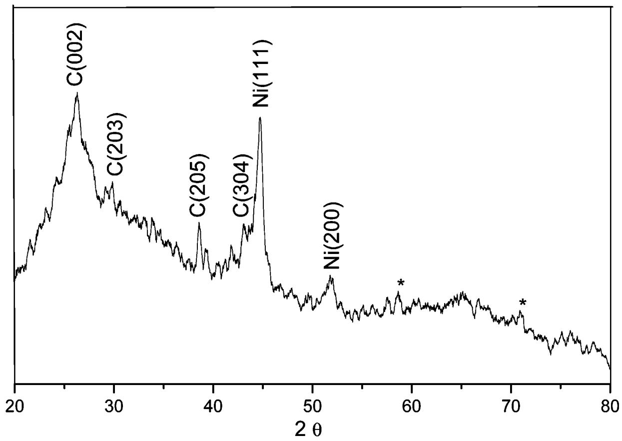

Fig. 2 X-Ray diffraction pattern of the sample. The diffraction peaks of nickel carbide are indicated by asterisks.

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22-1069. From these analyses we can see that pyrolysis of C_2H_2 on the array of Ni nanotubes at 650 °C yields a novel nanostructure of Ni nanotubes encapsulated in carbon nanotubes. In Fig. 1A and B, there are many dark spots around the nanostructure of the C/Ni tube-in-tube structure, which is composed of carbon only as established by EDS. Two very important features can be seen from Fig. 1: (i) compared with the original nickel nanotubes (about 160 ± 20 nm diameter), the diameters of the nickel nanotubes become smaller (40–90 nm) after the catalytic pyrolysis reaction and (ii) the carbon nanotubes were formed on the outer surface, which are originally in close contact with the alumina membrane rather than the interior surface of the Ni nanotubes (Fig. 3). This is a very interesting phenomenon and may help us to understand the formation mechanism of the carbon nanotubes. In addition, the diameter of the carbon nanotubes is in the range 180–220 nm, corresponding to that of the pores of the alumina membrane.

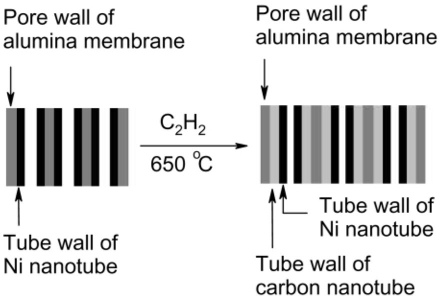

Fig. 3 Schematic of the change in nanostructure after decomposition of C_2H_2 on the array of Ni nanotubes in the membrane support.

Carbon nanotubes have been prepared *via* decomposition of C_2H_4 or C_2H_2 on Fe, Co or Ni/support. These studies have revealed that the presence of transition metal particles is essential for the formation of carbon nanotubes. Two growth modes of carbon nanotubes have been found: tip- and root-growth modes.[2,14] In our experiment, although Ni retains its tubular structure after the catalytic reaction, its diameter is significantly smaller than before the reaction. Furthermore carbon nanotubes did not form along the interior surface of the Ni nanotubes. This indicates a different carbon growth mode from the tip- and root-growth observed previously. We propose that the pyrolysis of C_2H_2 on the array of Ni nanotubes is comprised of two steps. First, the hydrocarbon decomposes on the interior surface of the Ni nanotubes followed by diffusing to the Ni lattice to form a carbide eutectic. Second, the carbide decomposes into carbon and Ni *via* a solution–precipitation mechanism and the carbon permeates through the wall of the Ni nanotube and grows on the outer surface of the Ni nanotube.[15] The Ni from the decomposition of nickel carbide then reforms a tubular structure again. As the nickel carbide forms and decomposes repeatedly, the wall thickness of the carbon nanotube increases gradually and, due to the force from the increasing wall thickness of the carbon nanotubes, the diameter of the reformed nickel nanotubes decreases gradually. The diameter of the Ni nanotubes in the composite nanostructure is thus smaller than that of the original Ni nanotubes. This hypothesis can be further confirmed from the XRD which shows several small diffraction peaks of nickel carbide (Fig. 2, marked as asterisks) in addition to carbon and nickel diffraction peaks. Also, there is a different nanostructure on the end of the Ni nanotube, which follows the root-growth mode and forms a hollow carbon nanotube in that area (Fig. 4).

In summary, a novel nanostructure of Ni nanotubes encapsulated in carbon nanotubes has been obtained *via* the pyrolysis of

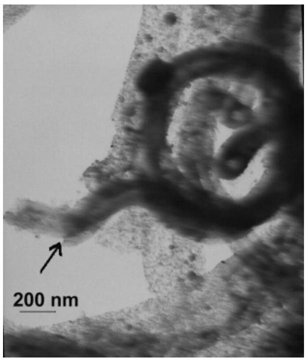

Fig. 4 TEM image of a sample prepared by decomposition of C_2H_2 on an array of Ni nanotubes, showing a carbon nanotube growing at the end of the Ni nanotube (arrowed).

C_2H_2 on an array of Ni nanotubes. It is important to note that the Ni retains its tubular structure but that the diameter of the Ni nanotubes becomes smaller after the catalytic pyrolysis reaction. This phenomenon gives an insight into the formation mechanism of the carbon nanotubes. A possible mechanism has been proposed. To the best of our knowledge, such a novel nanostructure of nickel nanotubes encapsulated in carbon nanotubes has not been reported previously[6–8] and might have many potential applications in catalysis, field emission, electrochemical research and high-density magnetic memories, *etc*. Further work is under way to systematically study the magnetic and catalytic properties of the nanostructures.

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