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Super-long continuous Ni nanowires encapsulated in carbon nanotubes†

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Super-long continuous Ni-filled carbon nanotubes were synthesized by the chemical vapor deposition (CVD) method with cloth-like single-walled carbon nanotube (SWNT) raw soot produced by the arc-discharge method as catalyst; the Ni nanowires inside the carbon nanotubes are single crystals, with an average diameter of 40 nm and up to tens of micrometres in length.

Because of their unique electronic, optical, mechanical properties and potential applications in nano-electronics, one-dimensional (1D) nanomaterials have stimulated considerable attention in recent years.[1–4] Theoretical studies[5–6] suggested that introduction of foreign materials into hollow nanotubes' cavities may significantly modify their electronic and mechanical properties, as well as alter the properties of the filling materials. Since Ajayan[7] and his co-workers succeeded in opening and filling carbon nanotubes (CNTs) by heating them in air in the presence of molten Pb, various filling techniques, such as capillary action,[8a] the wet chemical method,[8b] the arc-discharge technique,[8c] and the electrochemical deposition method[8d] have been developed to fabricate solid nanowires by filling hollow cavities of CNTs with elements or compounds. Recently, Ajayan[9] and his co-workers reported an interesting phenomenon that single-walled carbon nanotube (SWNT) raw soot ignited after being exposed to a conventional photographic flash in ambient conditions. Bockrath *et al.*[10] suggested that the common feature of materials that ignite is the combination of well-dispersed metal catalyst nanoparticles in intimate contact with the high-surface area carbon nanotube. The finding may have implications for the utilization of metal nanoparticles embedded on carbon nanotubes as a catalyst for hydrocarbon pyrolysis. Here we describe a novel chemical vapor deposition (CVD) method for preparing high ratio Ni-filled carbon nanotubes by using the cloth-like SWNT raw soot as catalyst. The cloth-like raw soot containing nearly 30% SWNTs was produced by the arc-discharge method.[11] In a typical preparation, 100 mg cloth-like raw soot with a smooth surface was placed in a quartz boat inside a quartz tube (id 30 mm) reactor and the temperature of the reactor was increased to 850 °C under a flowing gas composed of H_2 15 sccm, Ar 250 sccm. When the temperature got to 850 °C, a source of 150 sccm flow of methane and 15 sccm flow of hydrogen was passed through the quartz reactor tube for 30 min. Subsequently, the source gas stream was switched to Ar at a flow rate of 250 sccm and naturally cooled down to room temperature. After the CVD process, there were some brushy materials on the smooth surface of the cloth-like raw soot and the whole product (including the original cloth-like raw soot) weighed 130 mg. Typical SEM images of the cloth-like raw soot and the brushy materials are shown in supplementary information.† From transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) characterization, there are Ni-filled multi-walled carbon nanotubes in these brushy materials. The Ni nanowires inside the MWNTs have an average diameter of 40 nm and lengths of up to tens of micrometres.

Fig. 1a shows the TEM image (JEOL 200CX, working at 120 kV) of the cloth-like raw soot obtained from the arc-discharge method. A network of SWNT bundles is clearly visible along with some amorphous and nanocrystalline carbon. In addition, Ni nanoparticles with different diameters, originally used as the catalyst for production of the SWNTs, appear embedded within the bundles, which is similar to that found in our previous report.[11] The result of differential scanning calorimetry (DSC) (Netzsch Sta 449C with Ar as carrying gas) experiments on the cloth-like raw soot is shown in Fig. 1b, which indicates that melting of Ni nanoparticles occurs in a broad range, from 700 °C to 1200 °C. The DSC results confirm that the Ni nanoparticles embedded on the SWNTs' surface share a broad range of diameters. These lower melting-point nanosized metal particles should have higher reactivity than their bulk counterparts.

The X-ray powder diffraction (XRD) patterns (Rigaku D/max diffractometer with Cu Ka radiation) of the sample before and after the CVD process are shown in Fig. 2. Before the CVD process, face-centered cubic (fcc) Ni is the dominant peak and only a weak graphitic peak, which is ascribed to the nanocrystalline carbon, could be seen. After the CVD process, the (002) graphitic peak, corresponding to a graphite type of structural arrangement, becomes more prominent. This result proves MWNTs are formed in the CVD process. When the powder isdispersed in concentrated HCl (12 M), most of the Ni particles dissolve. The (002) graphite

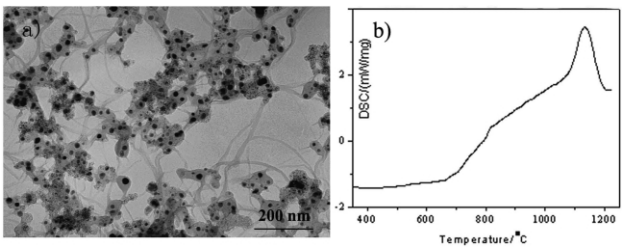

Fig. 1 (a) A typical TEM image of the cloth-like raw soot from the arc-discharge; (b) DSC curve of the cloth-like raw soot.

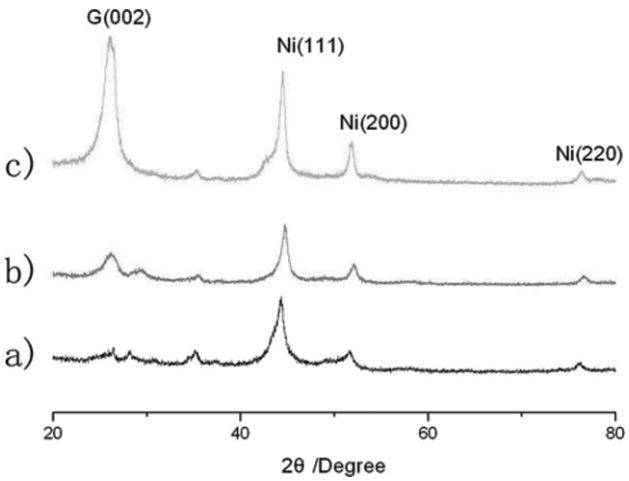

Fig. 2 X-Ray diffraction patterns of the samples: (a) the cloth-like raw root from the arc-discharge apparatus; (b) after CVD process; (c) after treatment with 12 M HCl.

† Electronic supplementary information (ESI) available: SEM images. See http://www.rsc.org/suppdata/cc/b4/b405444j/

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peak becomes the dominant peak, along with the encapsulated fcc Ni peaks.

Fig. 3a and 3b are TEM images of Ni-filled carbon nanotube composite nanostructures. From the figure, there is only trace impurity attached to the smooth surface of the CNT, whose length can extend to tens of micrometres without any tangling. The product displays a coherent darker contrast center core than the outer layer along the tube axis direction, indicating that the CNT is completely filled with metal. The outer diameter and the wall thickness of the nanotube are ~70 nm and ~15 nm, respectively, and the diameter of the central metal nanowire is ~40 nm. With the energy dispersive X-ray (EDX) spectral analyzer installed in the TEM, the component of the metallic nanowire in the CNT was determined to be Ni (Fig. 3c). The Cu signals were due to the copper grid supporting the sample.

In order to determine the materials inside the CNTs in detail, their structures were analyzed by means of selected area electron diffraction (SAED). The corresponding SAED pattern (Fig. 3d) of the Ni-filled CNT nanowire taken from Fig. 3b does not change along the length of the wire, while the intensity of the individual spots show a slight variation. The brightest arc corresponded to the (002) reflection of hexagonal graphite and the sharp spots could be indexed by considering the face-centered cubic (fcc) Ni structure. Therefore, the crystalline core is fcc Ni with the $\langle 011 \rangle$ axis parallel to the electron beam, and the growth orientation of this wire is along the $[0\bar{1}1]$ orientation.

Fig. 4 shows a HRTEM (Philips Tecnai-F30, working at 300 kV) image of a typical 40 nm diameter Ni nanowire encapsulated in a CNT. Long single-crystal has been observed. Lattice fringes from the sheath (left) indicate that the interlayer distance is ~0.35 nm,

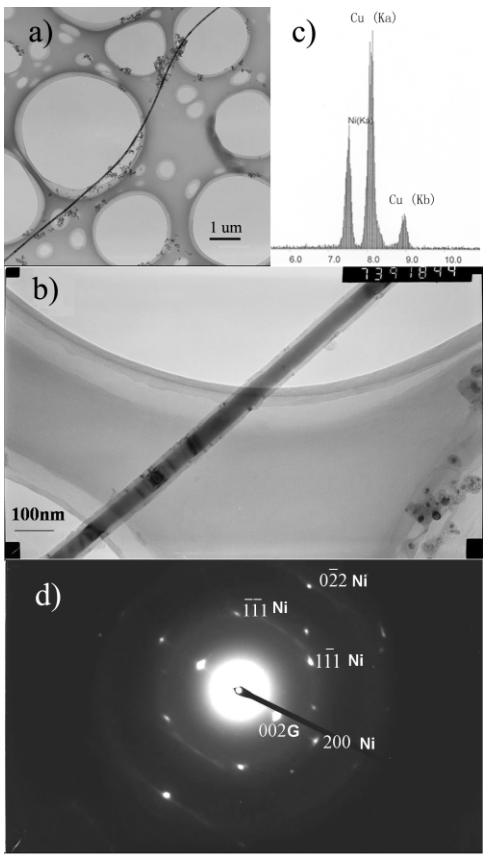

Fig. 3 TEM of Ni-filled carbon nanotube nanostructures : (a) low magnification; (b) high magnification; (c) EDX of this typical Ni filled MWNT; (d) SAED of this Ni filled MWNT.

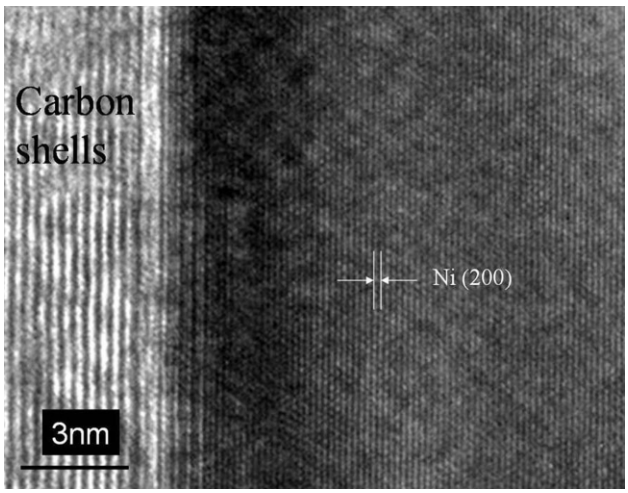

Fig. 4 HRTEM image of a Ni-filled carbon nanotube.

near the (002) spacing of graphitic carbon. From the crystalline Ni core (right), we can see the typical $\langle 011 \rangle$ projection of fcc Ni structure with (200) plane spacing of ~0.17 nm. The lattice (200) plane fringes of fcc Ni run parallel to the (002) fringes of the CNT, and the growth orientation of this wire is along the $[0\bar{1}1]$ orientation. We randomly checked several of these encapsulated Ni nanowires, all of them showed $[0\bar{1}1]$ orientation. The synthesis mechanism of this hybrid material is open to question; we propose that when these nanotubes grew, Ni was sucked into the core of the nanotubes through capillary action.

In summary, we have presented a novel CVD method to synthesize multi-walled carbon nanotubes filled with ultra-long continuous Ni nanowires by using cloth-like SWNT raw soot as catalyst. The nickel nanowires encapsulated in the carbon nanotubes are single crystals, with an average diameter of 40 nm and are tens of micrometres in length. The growth orientation of this Ni wire is along the preferred $[0\bar{1}1]$ orientation. The carbon nanotubes filled with metal possess potential applications in nanotechnology. Metal nanowires with novel physical properties may in principle be manufactured by removing the carbon layer.

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