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Synthesis of $CoFe_2O_4$ nanowire in carbon nanotubes. A new use of the confinement effect†

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Cobalt ferrite nanowires with an average diameter of 50 nm and lengths up to several micrometers were synthesized inside carbon nanotubes under mild reaction conditions using the confinement effect provided by the carbon tubular template.

Since the discovery of carbon nanotubes using the arc discharge method,[1] an increasing interest has been devoted to the preparation of metal or metal nanocluster filled carbon nanotubes or related materials for potential applications in nanoelectronic, catalytic or magnetic devices.[2,3] Ajayan *et al.* used the surface-tension effect to fill carbon nanotubes with vanadium oxide at relatively high filling temperature, *i.e.* 1023 K.[4] However, it should be stressed that the filling selectivity remained relatively low, filled and externally coated carbon nanotubes both being present in the final sample. Recently, Xu *et al.* have reported the filling of single-walled carbon nanotubes with lanthanide halide by heating an intimate mixture of carbon nanotubes and halide above the melting point of this halide.[5] However, the high yield filling of carbon nanotubes by foreign nanowires with length greater than nanometers, under mild conditions, still remains a difficult goal which numerous groups are trying to attain.[6]

We report here a new use of the confinement effect concept, provided by the carbon tubular morphology, the extremely high mechanical strength of which allows encapsulated nanowires up to micrometer length to be prepared under relatively mild synthesis conditions and with a high filling yield without formation of the foreign compound outside the tubes. This confinement concept is illustrated by the synthesis of the spinel $CoFe_2O_4$ mixed oxide which is an interesting and well studied magnetic compound. The ability to prepare highly anisotropic $CoFe_2O_4$ in nanowire shape could allow the easy alignment of such a material, *i.e.* perpendicularly with respect to a support surface, for possible use in magnetic recorders or data storage media. It is also worth noting that the surrounding carbon wall is expected to prevent the dipolar relaxation between two neighbouring magnetic centres and to avoid the sintering of nanoparticles during the shaping of the material, which are both major drawbacks of classical spinel nanoparticles.

Open carbon nanotubes with a mean outer diameter of 120 nm, a mean inner diameter of 60 nm and lengths up to several micrometers were supplied by Applied Sciences Ltd. (Ohio, USA) and used as received. The carbon nanotube filling process was performed as follows: the metal precursor salts ($Fe(NO_3)_3$ and $Co(NO_3)_2$ with a molar ratio of 2 : 1 and a metal content of 30 wt% relative to the carbon nanotubes) were first dissolved in a volume of distilled water (60 ml) corresponding to the inner volume of the carbon tubules, previously determined by analysis of a statistical sample of microscopy images. The nanotubes (10 g) were subsequently immersed in the solution under vigorous stirring.

During the impregnation process, the carbon nanotubes were rapidly filled with the aqueous nitrate solution due to capillary forces. This was possible because the surface tension of water (72 mN m^{-1}) is, according to the literature, sufficiently low (*i.e.* $<$ 190 mN m^{-1}) to allow wetting and filling of nanotubes.[7] A transmission electron microscopy (TEM) image after overnight air treatment at 323 K shows the presence of solid caps composed of Co, Fe, O elements (obtained by energy dispersive X-ray spectroscopy, EDS), together with gas bubbles and/or liquid remaining trapped inside the tube (Fig. 1(a)). A part of the

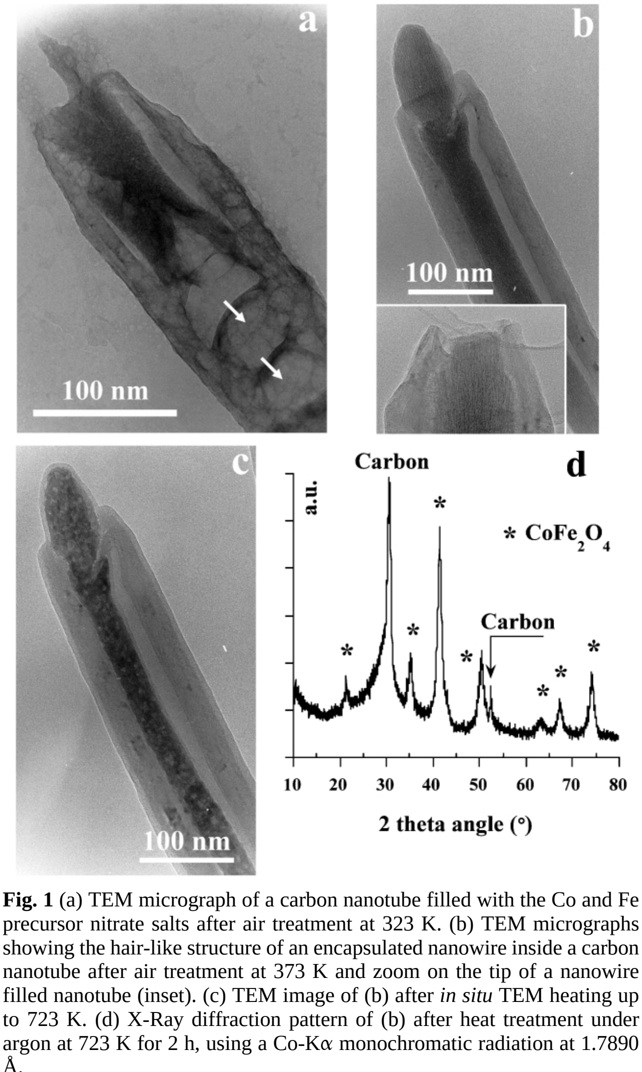

Fig. 1 (a) TEM micrograph of a carbon nanotube filled with the Co and Fe precursor nitrate salts after air treatment at 323 K. (b) TEM micrographs showing the hair-like structure of an encapsulated nanowire inside a carbon nanotube after air treatment at 373 K and zoom on the tip of a nanowire filled nanotube (inset). (c) TEM image of (b) after *in situ* TEM heating up to 723 K. (d) X-Ray diffraction pattern of (b) after heat treatment under argon at 723 K for 2 h, using a Co-Kα monochromatic radiation at 1.7890 Å.

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† Electronic supplementary information (ESI) available: XRD patterns and TGA traces. See http://www.rsc.org/suppdata/cc/b2/b203787b/

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liquid nitrate precursor first decomposed near the tube tip during the heating at 323 K leading to the formation of solid caps at the tube tips. The remainder of the nitrate precursor remained caught inside the tube, blocked by the solid caps, as evidenced by the arrows in Fig. 1(a). The XRD pattern (not reported) only showed diffraction lines corresponding to the carbon support phase and those originating from the nitrate phases were not observed. A similar impregnation method carried out on SiC nanotubes with a different surface nature only led to the decoration of the SiC tubes with $CoFe_2O_4$ particles.[8] On this sample, the XRD pattern recorded after heating in air at 373 K clearly showed the presence of nitrate phases. This observation is in line with the general concensus that the nitrate precursor is not transformed or decomposed at such a low temperature without a participation of a confinement effect. The TEM image of the sample after further overnight air treatment at 373 K, evidenced the presence of a solid phase containing Co, Fe and O, exclusively located inside the carbon nanotubes in the form of long hair-like nanowires, with a length up to several micrometers and a diameter corresponding to that of the inner diameter of the host tubes (Fig. 1(b)). Such a long filling length was significantly higher than that previously reported for filled carbon nanotubes.[3,6] The stoichiometry of this encapsulated solid phase, obtained by semi-quantitative decomposition of the EDS spectrum, was close to that of $CoFe_2O_4$. Further *in situ* heating of the material up to 723 K resulted in the formation of small particles, while the nanowire morphology was retained (Fig. 1(c)). Mössbauer analysis performed at 4.2 K (Fig. 2(a)) proved that the formation of the $CoFe_2O_4$ phase already occurred after air treatment at 373 K, what could not be accurately observed by other techniques such as X-ray diffraction (XRD) due to a too small particle size. The typical signature of the $CoFe_2O_4$ spinel phase with two hyperfine sextets, corresponding to iron ions in both octahedral and tetrahedral cristallographic sites, was observed.[9] *Ex situ* argon treatment at 723 K led to small spinel mixed-oxide particles (10 nm), without additional oxygen having been required and however big enough to be detected by XRD (Fig. 1(d)). During the temperature increase (from 373 to 723 K, *in* or *ex situ*, *ex situ* heating being necessary to obtain gram quantities of products), the presence of caps leads to a pressure increase inside the tubes, similar to that involved in hydrothermal synthesis of zeolites or other oxides.[10,11]

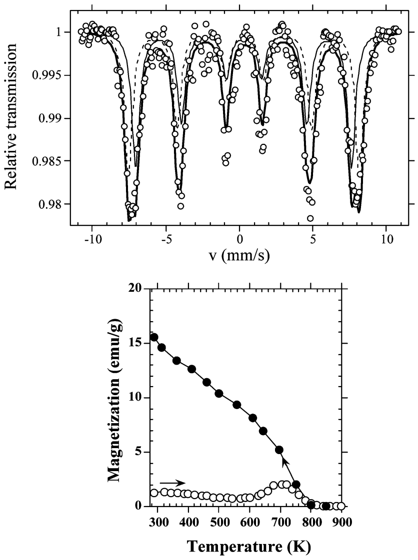

Fig. 2 (a) Mössbauer spectrum recorded at 4.2 K on the nanowires filling carbon nanotubes sample after air treatment at 375 K. Experimental points (○), iron ions in octahedral (···) and tetrahedral (—) sites and the resulting fit (—). (b) Magnetization evolution as a function of the temperature under flowing air with an applied field of 0.5 T on the nanowires filling carbon nanotubes after air treatment at 373 K. Increasing temperature (○) and decreasing temperature (●).

The transformation of the iron and cobalt nitrate salts, trapped inside the carbon nanotubes, into the corresponding oxidic spinel structure under mild conditions was expected to be helped by the surrounding tube walls, according to the concept of a nanoreactor, *i.e.* confinement medium. The carbon nanotubes acted as a nanoreactor and this concept is based on the differentiation between the synthesis parameters inside and outside the tubes: the macroscopic pressure remained unchanged outside the tubes, while the nanoscopic pressure increased inside. This was in close agreement with the results recently reported by Gogotsi *et al.*, who demonstrated the ability of carbon nanotubes with an outer diameter of 100 nm to act as miniature pressure vessels and to retain pressurized fluid, also confirming the high strength of such nanostructures.[12]

$CoFe_2O_4$ formation was confirmed by magnetic measurements, the nanowires exhibiting a Curie temperature of about 780–800 K, in close agreement with that reported in the literature for the $CoFe_2O_4$ spinel phase (Fig. 2(b)).[9,13] The lack of magnetization at temperatures lower than 600 K is attributed to the rapid relaxation of the magnetic moments due to the high surface-to-volume ratio of the dentritic amorphous or very highly dispersed phase located inside the tubes. The large increase in magnetization when the temperature was raised from 600 to 700 K is attributed to the increase in the $CoFe_2O_4$ structural order and in turn its particle size. The strong increase in magnetization during the subsequent cooling to room temperature (*i.e.* lower than the Curie temperature) confirmed the $CoFe_2O_4$ formation. The magnetization after air treatment at 723 K for 6 h reached 30 emu g^{-1} at room temperature (not shown) for an applied field of 5 T (*i.e.* about 77 emu g^{-1} of ferrite taking into account the metal loading), in close agreement with that reported in the literature for bulk $CoFe_2O_4$,[9,13] with no saturation indicating that the particles remained small.

In conclusion, multi-walled carbon nanotubes as suitable hosts for nanowire synthesis raise the exciting possibility of using such open nanostructures as nanoscale reaction vessels.[14] Using the confinement effect provided by the carbon nanotubes and thus acting as nanoreactors, several hundred nanometer length nanowires of spinel $CoFe_2O_4$ were synthesized at atmospheric pressure and at low temperatures. Up to now no reports have dealt with the synthesis of such compounds with nanowire morphology under such mild conditions.

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