MAGNETO-TRANSPORT IN CARBON-NANOTUBE-TEMPLATED 1D-COBALT-CRYSTALS

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Introduction

Carbon nanotubes may need to be modified to enhance their properties or get new ones, and access a wider variety of applications. There are five different ways to modify carbon nanotubes – so-called meta-nanotubes: substituting, coating, functionalising, doping, and filling [1-2]. Filled nanotubes are probably the kind of meta-nanotubes offering the widest versatility regarding the range of properties and applications likely to be opened by tailoring the chemical, structural, and morphological nature of the filling material, as well as the type of carbon nanotubes to be filled. For instance, chances for enforcing new lattice structures of the filling material are higher inside single-walled carbon nanotubes (SWNTs) than inside multi-walled carbon nanotubes (MWNTs), due to higher sterical constrain conditions. In this study, we have focused on filling small diameter (~1.4 nm) SWNTs with metallic cobalt, aiming to reveal any peculiar magneto-transport behaviour that might be exhibited by such a presumably conductive and ferromagnetic material when dimensionally reduced down to the size of a quantum wire.

Experimental

Purified and opened arc-prepared SWNTs (supplier: Nanocarblab, Russia) whose diameters mostly range from ~0.9 to ~1.8 nm with a mode at 1.35 nm were filled with cobalt following the "melting" path of the liquid phase route (Figure 1). As the

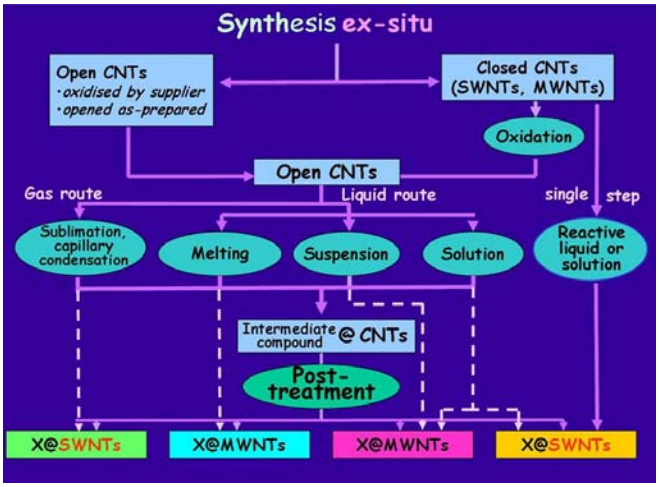

Fig. 1: The various filling strategy for the synthesis of hybrid (filled) carbon nanotubes [1-2].

melting temperature of cobalt was too high, we started from cobalt iodide CoI_2 (see ref. 127 in [2]) and mixed it in excess with SWNTs in a pre-vacuumed, sealed quartz ampoule subsequently heated up to 550 °C for 24 hours. CoI_2@SWNT material was obtained, removed from the ampoule and washed with ethanol in order to remove the residual (non encapsulated) COI_2, and then reduced into Co@SWNTs by heating it at 400°C for 24 hours in H2/Ar (45/70 ml/min) atmosphere. The materials were checked by high resolution transmission electron microscopy (HR-TEM) at each step (Figure 2). Filling rate for the resulting Co@SWNT material was not better than ~20%, as estimated by HR-TEM.

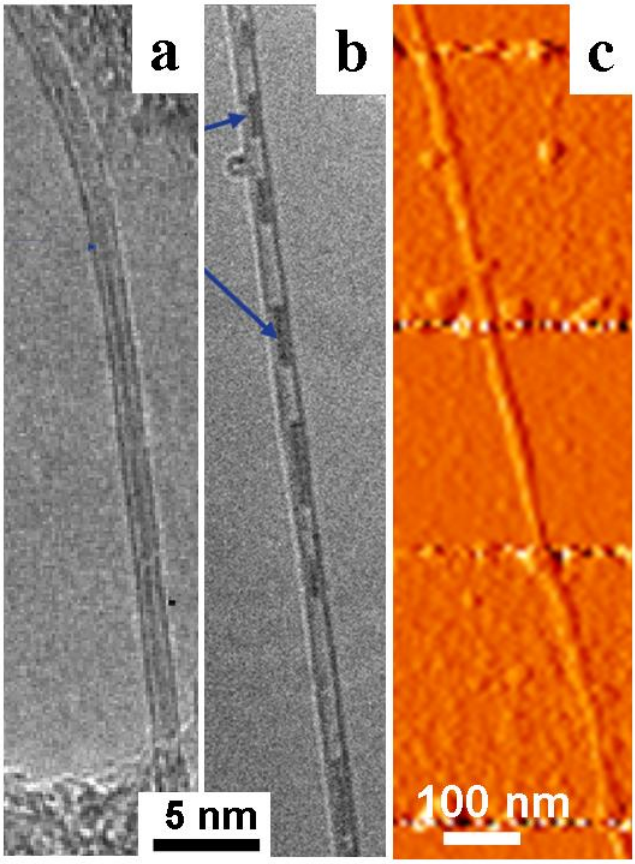

Fig. 2: TEM image of (a) an example of a single CoI_2@SWNT, here filled over a length of several tens of nanometers; (b) an example of a single Co@SWNT, obtained from hydrogen reduction of the former. The sequential and somewhat periodic feature of the filling is a common observation. (c) AFM image of a bundle supposedly containing some Co@SWNTs contacted with 50 nm thick palladium pads.

A highly diluted solution of the Co@SWNT material added with SDS surfactant was then prepared and microdroplets of it were deposited in the central zone of a Si-doped wafer substrate pre-patterned with photo-lithographed gold contacts. The area was then scanned by atomic force microscopy (AFM) in order to select the nanotubes to be subsequently contacted (with Pd) by electron lithography according to the standard transistor configuration. Isolated nanotubes as shown in Figures 2a and 2b were scarce, and mostly small bundles were contacted (Figure 2c). Because the Si wafer is not electron transparent, it was

impossible neither to determine the number of SWNTs nor to check the extent of filling in the contacted bundles.

Voltage-current measurements were carried-out at 40 mK on ~80 devices using variable back-gate voltage (~ -5 V < V_g < 0) and increasing-decreasing magnetic field cycles (~ -3 T < $\mu_0 H$ < 3 T) at ~70 mT/s. Other parameters were the polarization current and the angle between the magnetic field and the bundle long axis.

Results and Discussion

For 90% of the devices, the conductance varies continuously along the magnetic filed cycle and symmetrically with respect to the zero field situation, without exhibiting any hysteresis (Figure 3a), yet showing variations whose interpretation is not ascertained. They may relate to the presence of defects and/or impurities and/or to some contribution of a Zeeman effect (see below) for instance.

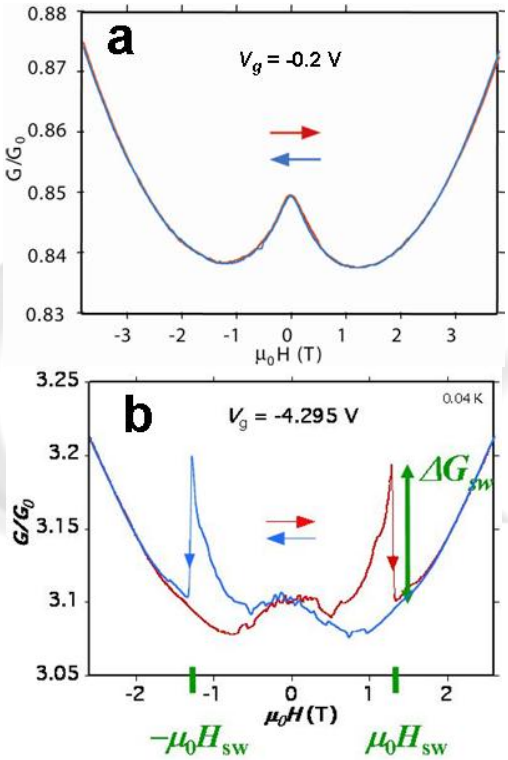

Fig. 3: Variation of conductance versus cycling magnetic field; (a) Example of a no-hysteresis case (most frequent); (b) Example of a hysteresis case, for an angle of 25° between the direction of the magnetic field and the elongation axis of the bundle.

For ~10% of the devices, however, the conductance *vs* magnetic field curve exhibits a hysteresis with two conductance jumps. They correspond to the magnetic field value at which the magnetisation direction of a nano-magnet (presumably one - or several, but aligned - encapsulated cobalt wire segment(s)) reverses. Varying the back gate voltage only results in modifying the jump amplitude and/or direction but does not affect the switching field value $\pm\mu_0 H_{SW}$. Such a modification of the transport of electrons through a conductor (here: the SWNTs, since the distance between two contacts is by far larger than the average lengths of the encapsulated cobalt nanorods) by the magnetization state of a magnet electronically coupled to it is known as a Magneto-Coulomb effect. Here, it is interpreted as a consequence of the so-called Zeeman effect, which describes that, when a magnetic field is applied in a direction parallel to the preferred magnetization axis of a nano-magnet, the potential energy of the latter changes linearly. In Co@SWNT bundles, since the nanomagnets are encapsulated in SWNTs, the Zeeman energy also modifies the chemical potential of the latter, which appears as a variation of the effective charge ΔQ. As ΔQ is proportional to the applied magnetic field, it increases continuously as the field increases, until the Co nanomagnets reverse their magnetisation direction. This event induces a discontinuity in the variation of ΔQ which results in a conductance jump.

Another interesting result is the evidence that, as opposed to what happens with larger (~10-50 nm in diameter), ferromagnetic crystals encapsulated in MWNTs [3], the preferred magnetisation axis of our cobalt nanorods encapsulated in SWNTs was found to be perpendicular to the elongation axis. This reveals that the surface magnetocrystalline anisotropy prevails over the shape anisotropy [4-5], due to the large fraction of surface atoms in the ~1 nm large cobalt crystals.

Finally, the value for the switching field was found to decrease as the temperature increases. Hence, extrapolating the plot down to a zero field situation allowed the temperature beyond which the magnetisation reversal may no longer occur to be calculated (12 K).

Conclusions

SWNTs provide an attractive one-dimensional system for molecular spintronics devices. When magnetic compounds are electronically coupled to conducting SWNTs, a Magneto-Coulomb effect may occur which makes the low temperature transport of electrons through the SWNTs be influenced by the magnetization state of the magnets. Filling SWNTs with cobalt nanoparticles has allowed such behaviour to be evidenced by conductance jumps which relate to the magnetisation reversal of the encapsulated cobalt nanorods. The study has established the dominating contribution of magnetic surface anisotropy, and the control of the jump amplitude and direction by the grid voltage.

References

[1] Monthioux, M., Flahaut, E., Cleuziou, J.P. Hybrid carbon nanotubes : Strategy, progress and perspectives. J. Mater. Res. 2006;21:2774-2793.

[2] Monthioux M., Flahaut E. Meta-and hybrid-CNTs: a clue for the future development of carbon nanotubes. Mater. Sci. Eng. C 2007;27: 1996-2101.

[3] Kozhuharova, R. *et al.* Well-aligned Co-filled carbon nanotubes: preparation and magnetic properties. Appl. Surf. Sci. 2004;238:355-359.

[4] Allenspach, R., Stampanoni, M., Bischof, A. Magnetic domains in thin epitaxial Co/Au(111) films. Phys. Rev. Lett. 1990;65:3344-3347.

[5] Jamet, M. *et al.* Magnetic anisotropy of a single cobalt nanocluster. Phys. Rev. Lett. 2001;86:4676.