Synthesis and crystal structure of single-walled carbon nanotubes filled with ruthenium compounds

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Motivation

Low - dimensional magnetic halides have gathered considerable attention due to their promising optical properties and diverse magnetic behaviour in such form. Reduced dimensionality is likely to elevate the magnetic Neel (T_N) and Curie (T_C) transition temperatures which is certainly an appealing prospect in their investigation [1]. Utilizing single-walled carbon nanotubes (SWCNTs) as "nano-templates" for growth of magnetic halides crystals provides strong spacial confinement which not only allows to obtain the lowered dimensionality of the grown materials but also often imposes their novel crystallography and modifies the stoichometry [2]. α-$RuCl_3$ is an antiferromagnet with a zig-zag ordering below $T_N \approx 7$K but it has been reported that its transition temperature can be elevated up to 14K due to the stacking faults in the chloride's layered structure [3]. It clearly shows that a modification of α-$RuCl_3$ structure has an impact on its magnetic behaviour.

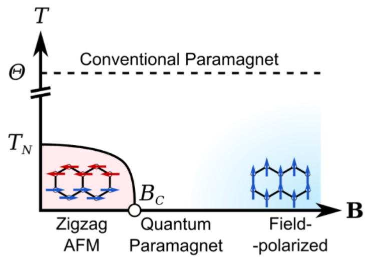

Fig.1 Schematic magnetic phase diagram of single-crystal α-$RuCl_3$ with field applied in the honeycomb *ab* plane (**H** ⊥ **c**) [4].

Experimental

Filling of the nanotubes generally can be performed in two ways - either using the **melt filling method** or the **resublimation method**.
- In the first one the mixture of the SWCNTs and the filling material is heated slightly above the latter's melting point and the nanotubes are filled thanks to the capillary mechanism.
- The second one uses gradient of temperature thanks to which the fillling material can sublimate in the hot zone and resublimate in the cold zone containing the SWCNTs and thus fill them.

Different mechanisms allow to adjust the technique to the type of filling material. During this research both of the methods were tried and led to different results.

Pre-processing of the SWCNTs

Comercially available SWCNTs are often contaminated with Fe, Co or Ni nanoparticles - residual catalysts from the nanotubes growth process. Such impurities are highly undesirable due to their ferromagnetic interference in further magnetic studies of the obtained nanocomposites. Therefore a purification protocol needs to be used in order to obtain clean nanotubes before using them for crystal growth. A protocol used here consists of three main parts: (I) heating the SWCNTs in 500°C for 1 hour in order to activate the tubes (by opening the ends), (II) acid treatment of the activated SWCNTs and (III) magnetic separation of the residual contaminated SWCNTs. The protocol has been found here [5] and got slightly modified and adjusted to the requirements of SWCNTs used in this project.

Step I - heating (activation)

T = 500°C, t = 1 h in tube furnace (air atmosphere)

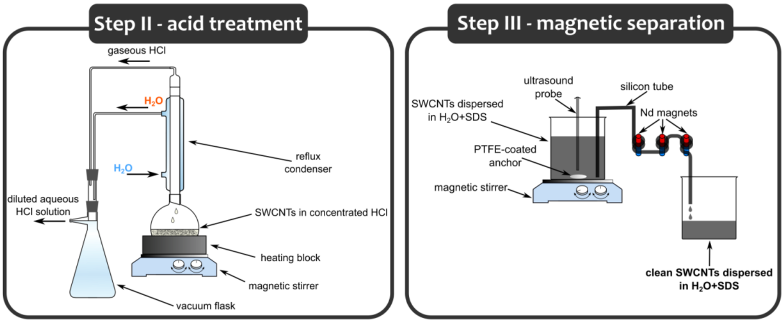

Fig.2 Schematic depiction of multistep purification protocol of single-walled carbon nanotubes.

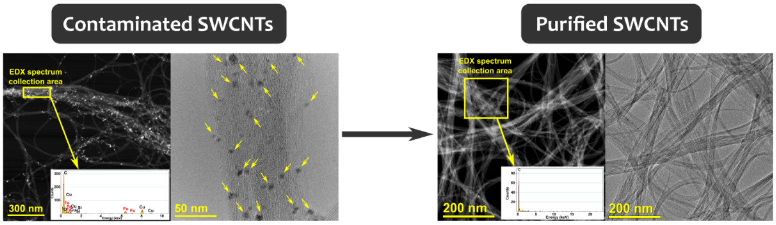

Fig.3 Comparison of STEM and HRTEM images complemented with EDX spectra of SWCNTs before (left panel) and after (right panel) the multistep purification process.

Results and conclusions

Melt filling

For the melt filling approach bulk $RuCl_3$ was grinded with purified SWCNTs in an agate mortar. The resulting mixture was vacuumized and sealed in a quartz ampoule. The ampoule was then placed in a tube furnace and heated to 600°C with a heating rate 1°C/min, kept in it for 7 days and after that cooled down with a cooling rate 1°C/min.

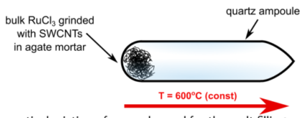

Fig. 4 Schematic depiction of ampoule used for the melt filling process.

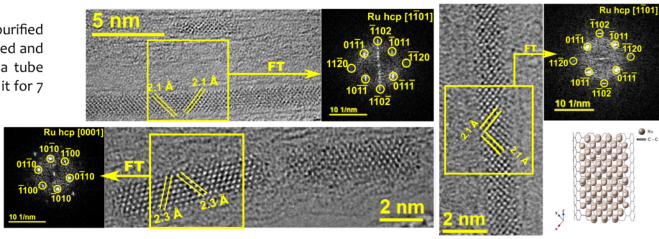

Fig. 5 HRTEM analysis of nanotubes filled with melt filling technique.
The analysis of HRTEM images showed that majority of the observed SWCNTs were filled with metallic Ru, which is a product of decomposition of $RuCl_3$.

It shows that this method is not good for this filling material - $RuCl_3$ decomposes instead of melting, thus cannot fill the nanotubes.

Resublimation filling

For the resublimation filling approach a modified type of ampoule was used - containing a narrowing preventing the SWCNTs from falling too close to the bulk filling material. The ampoule with reagents placed as shown in Fig. 6 was then vacuumized, sealed and placed in a tube furnace in such way to provide 200°C temperature gradient (Fig. 6). It was then heated with the heating rate 1°C/min, kept in the gradient for 14 days and cooled down with a cooling rate of 1°C/min.

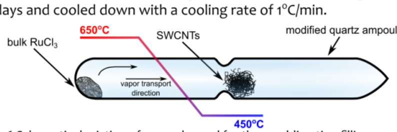

Fig. 6 Schematic depiction of ampoule used for the resublimation filling process.

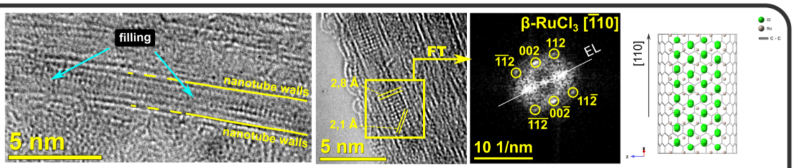

Fig. 7 HRTEM analysis of nanotubes filled with resublimation filling technique.

The analysis of HRTEM images showed that nanotubes were partially filled. Preliminary analysis of the filling shows that it is most probably β-$RuCl_3$ (hexagonal).

Resublimation method seems to be more suitable for this process - $RuCl_3$ can recrystallize in the cold zone of the ampoule but an overpressure of Cl_2 gas in the ampoule is needed to prevent the compound from decomposing to chlorine and metallic ruthenium.

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