Journal of Magnetism and Magnetic Materials 411 (2016) 39–48

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetism for understanding catalyst analysis of purified carbon nanotubes

Christine Bellouard [a], Guillaume Mercier [a], Sébastien Cahen [a], Jaafar Ghanbaja [a], Ghouti Medjahdi [a], Jérôme Gleize [b], Gianrico Lamura [c], Claire Hérold [a], Brigitte Vigolo [a,*]

[a] Institut Jean Lamour, CNRS-Université de Lorraine, BP 70239, 54506 Vandœuvre-lès-Nancy, France
[b] Laboratoire de Chimie Physique-Approche Multi-échelle de Milieux Complexes-Université de Lorraine, 1 Bd Arago, 57078 Metz, France
[c] CNR-SPIN – Dipartimento di Fisica, via Dodecaneso 33, 16146 Genova, Italy

ARTICLE INFO

Article history:
Received 31 January 2016
Received in revised form
14 March 2016
Accepted 15 March 2016
Available online 16 March 2016

Keywords:
Superparamagnetism
Spincrossover
Carbon nanotubes
Purification
Magnetization
Gas phase treatment

ABSTRACT

The precise quantification of catalyst residues in purified carbon nanotubes is often a major issue in view of any fundamental and/or applicative studies. More importantly, since the best CNTs are successfully grown with magnetic catalysts, their quantification becomes strictly necessary to better understand intrinsic properties of CNT. For these reasons, we have deeply analyzed the catalyst content remained in nickel–yttrium arc-discharge single walled carbon nanotubes purified by both a chlorine-gas phase and a standard acid-based treatment. The study focuses on Ni analysis which has been investigated by transmission electron microscopy, X-ray diffraction, thermogravimetry analysis, and magnetic measurements. In the case of the acid-based treatment, all quantifications result in a decrease of the nanocrystallized Ni by a factor of two. In the case of the halogen gas treatment, analysis and quantification of Ni content is less straightforward: a huge difference appears between X-ray diffraction and thermogravimetry results. Thanks to magnetic measurements, this disagreement is explained by the presence of Ni^{2+} ions, belonging to $NiCl_2$ formed during the Cl-based purification process. In particular, $NiCl_2$ compound appears under different magnetic/crystalline phases: paramagnetic or diamagnetic, or well intercalated in between carbon sheets with an ordered magnetic phase at low temperature.

1. Introduction

Carbon nanotubes (CNTs) and especially single walled carbon nanotubes (SWNTs) have remarkable intrinsic physical and chemical properties that make them as excellent candidates for fundamental studies and applications in many fields [1,2]. However, whatever the synthesis methods, as-produced CNT samples contain both secondary carbon products and metallic-based impurities involved in the growth mechanism as catalyst. They are often used in high content (10–30 wt%) in order to improve the nanotube formation and limit that of carbon byproducts. These metal-based impurities are reported to dramatically modify both chemical and physical properties of CNT [3–7]. Without any post-synthesis purification treatment, SWNTs become unusable because their intrinsic properties are lost or hidden due to the presence of these metallic particles. For this very reason, the development of purification treatments is a long-standing and active research area. Standard processes are often multi-step and generally combine (i) a reflux in concentrated nitric acid solution in order to weaken the carbon shells and oxidize the metal-based impurities (ii) a gas-phase or wet oxidation and (iii) a final annealing treatment to restore the defects created through previous steps [8–16]. More recently, high temperature treatment under halogens were evidenced as an interesting alternative technique to selectively remove metal-based impurities [17,18]. The assessment of the efficiency of such treatment indeed depends on the reliability of quantitative analysis of the remaining impurities. On one hand, local or surface analysis such as X-ray photoelectron spectroscopy or transmission electron microscopy (TEM) are used to determine their size and/or their chemical nature, however they are inefficient for a quantitative analysis [19]. On the other hand, macroscopic techniques such as thermogravimetry analysis (TGA) provide a quantitative analysis but without any discrimination regarding the chemical nature of the impurities in the purified samples. Among them, magnetic analysis (MAG) is a less commonly used technique [20–22]. It has been however shown to be very helpful to quantify magnetic residues from CNT samples [23-25]; especially because it is an ultrasensitive and non destructive method which can even detect very low amount of isolated paramagnetic impurities [19].

In this work, we have applied a Cl-based purification treatment on arc-discharged as-produced SWNTs under different temperature

* Corresponding author.
E-mail address: Brigitte.Vigolo@univ-lorraine.fr (B. Vigolo).

http://dx.doi.org/10.1016/j.jmmm.2016.03.056
0304-8853/

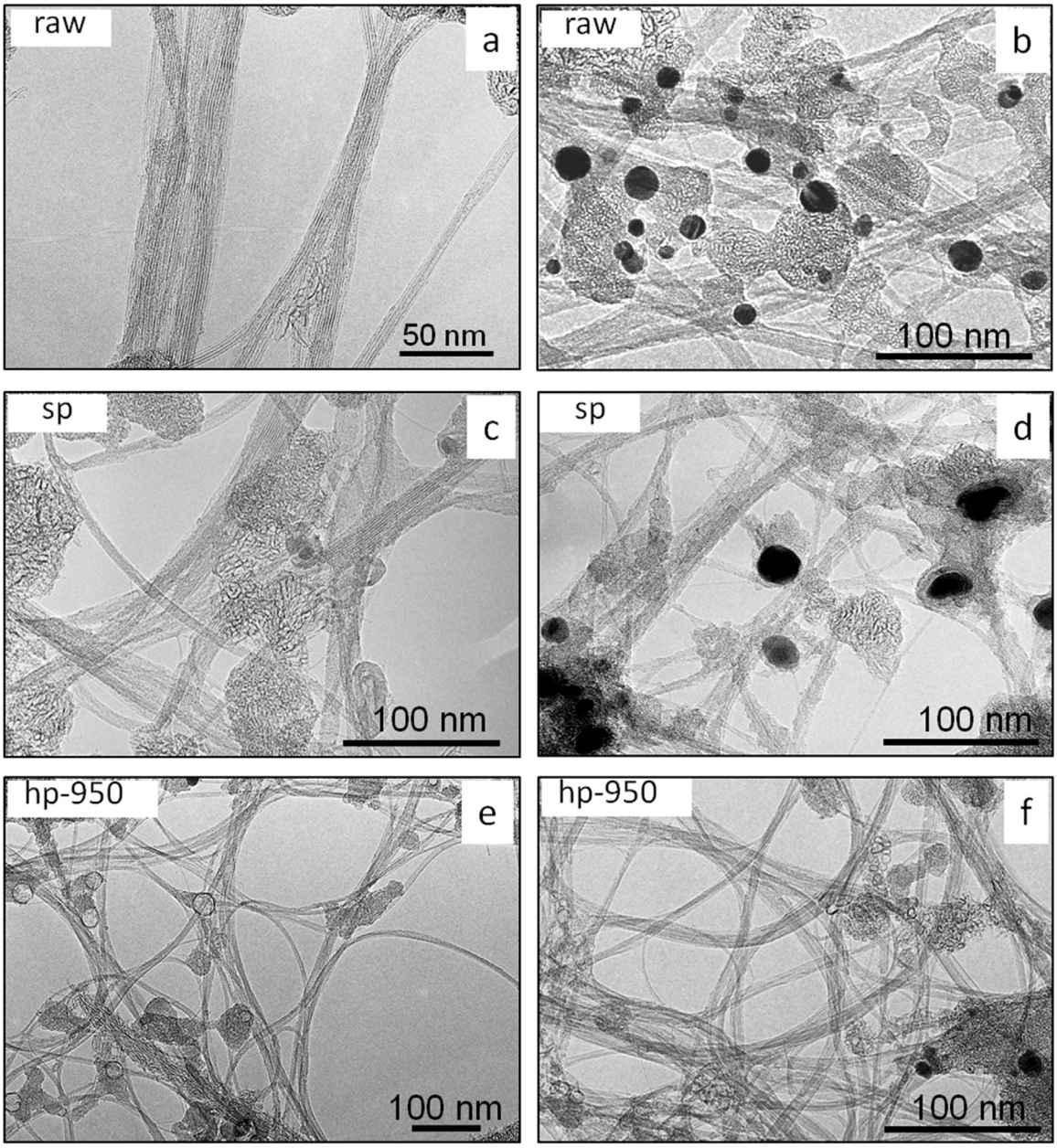

Fig. 1. TEM images of the raw sample, raw (a and b), a sample purified by a standard procedure, sp (c and d) and a sample purified by the chlorine-based process, hp-950 (e and f).

conditions. For comparison, a more standard purification method, based on an acid treatment has also been applied. Analysis and quantification of Ni-based impurities have been investigated by TEM, X-rays diffraction (XRD), TGA and MAG. A good agreement between TGA and MAG is found for the acid treatment whereas a strong deviation is observed between the results obtained from the different used techniques in the case of the Cl-based treatment. Thanks to magnetic measurements, these discrepancies are attributed to oxidation of Ni^0 into Ni^{2+} by the halogen gas. This result proves that chemical treatment used for purification can modify the impurity.

2. Experimental section

2.1. Sample preparation

The SWNTs used in this study have been synthesized in an arc-discharge homemade reactor described elsewhere [16]. The catalyst mixture is prepared with a graphite powder SFG6 (synthesized flake graphite 6 μm) from Timcal, nickel particles of around 3 μm purchased from Sigma Aldrich and yttrium powder (40 mesh) from Acros Organics. Ni/Y/C is fixed at 4.2/1/94.8 at% (2.8/1/96.2 wt%). The as-produced SWNT powder (referred as "raw") was purified using 2 different treatments: (i) a standard purification process that involves an oxidation under dry-air at 350 °C for 90 min, and a HCl (6N) reflux for 24 h followed by an annealing treatment under high vacuum (around 10^{-6} mbar) at 1100 °C for 60 min. The corresponding purified SWNT sample is referred as "sp". (ii) Heating under chlorine partial pressure of 0.9 atm (90% vol. of Cl_2 and 10% vol. of N_2, total pressure being 1 atm) for 2 h at 800 °C, 950 °C, or 1100 °C; and a washing with hydrochloric acid (4 N) is also performed at room temperature overnight to solubilize the possible remaining metal chloride formed during the reaction with chlorine [17]. After filtration, washing with pure water and drying, the purified SWNT samples at 800 °C, 950 °C, 1100 °C were assigned to "hp-800", "hp-950", "hp-1100", respectively.