



## C<sub>2</sub>H<sub>2</sub> interaction with Ni nanocrystals: Towards a better understanding of carbon nanotubes nucleation in CVD synthesis

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### ABSTRACT

We present a study of the early stages of carbon nanotubes nucleation in CVD synthesis by combining field ion/electron emission microscopy (FIM/FEM) and atom-probe investigation (AP) of the nickel–carbon interaction. Acetylene decomposition on Ni tips at 873 K is observed to induce additional step formation on an initially faceted (polyhedral) crystal. Carbon-enriched steps are then observed to act as preferential nucleation centers of graphene sheets formation. Atom-probe experiments reveal C<sub>2</sub> and C<sub>3</sub> species and frequency dependent studies demonstrate that the origin of these species is different from C<sub>1</sub>. Experiments provide clear evidence for the crucial role of carbon-enriched steps as nucleation sites of graphene sheets on the Ni surface.

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### 1. Introduction

Carbon nanotubes present outstanding physical and chemical properties which confer them a considerable potential for future industrial applications in numerous fields [1]. In this respect, the most widely used synthesis method is the Chemical Vapor Deposition process. It is based on the decomposition of a carbon containing gas (C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH or others) on a metallic catalyst (e.g., Ni, Co, Fe) at a temperature between 623 K and 1173 K, inducing direct growth of carbon filaments on the metal particles. CVD may provide high yields [2,3] and a relatively good control on several nanotubes characteristics (e.g., their diameter [4]) but the associated nucleation and growth mechanism is still strongly under debate. Some crucial features as, for example, the inherent chirality of nanotube structures are therefore not reproducibly acquired. For many years, the vapor–liquid–solid mechanism, or VLS [5], which involves dissolution of carbon in liquid metal particles up to supersaturation, was the most commonly accepted mechanism. Nevertheless, recent *in situ* TEM studies have questioned its validity at low temperatures [6–11] highlighting the solid state (and metallic for Ni) of metal particles during growth. Accurate *in situ* analysis of the particles morphology and composition during the nucleation and growth processes currently seems to be the most promising way to unravel this intense debate.

The present work is aimed at providing a new point of view to this question by studying nucleation-related phenomena using a combination of field ion and electron emission microscopy (FIM/

FEM) and atom-probe (AP) techniques. The application of these techniques provides structural and chemical information with (sub) nanoscale lateral resolution during the ongoing interaction of reactive gases with a sharp metal tip the extremity of which can be considered as an excellent model of a single catalyst grain. By using the microscope/atom-probe as a flow reactor, the early stages of the CVD process can thus be mimicked with high local magnification. In particular, carbon-induced morphological and topographical changes of Ni tips will be presented by exposing them to C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>OH at 623, 723 and 873 K. The carbon-induced formation of steps will be inspected along with association reactions between individual carbon atoms.

### 2. Experimental

For details of the principles of FIM/FEM and AP time-of-flight mass spectrometry see Ref. [12]. The application of these methods in heterogeneous catalysis has been recently described in detail [13]. Schemes of the atom-probe basic principles and of the device used in the present study are shown in Figs. 1(a) and (b), respectively. It has been designed to allow studying chemical surface reactions under dynamic gas pressures up to 10<sup>-2</sup> Pa. In particular, kinetic information can be gleaned by changing the field pulse repetition frequency, i.e., the reaction time between pulses [13]. Experiments were performed in a pure FEM/FIM and an FEM/FIM/AP combination device.

Ni tips were etched electrochemically from a high purity metal wire (99.994%, 0.1 mm dia.) in diluted HCl (0.5 mol/l) reaching ultimately ~10 nm radii of curvature. Welding grade acetylene (99.1% purity, further purified by passing through a dry ice cold-trap)

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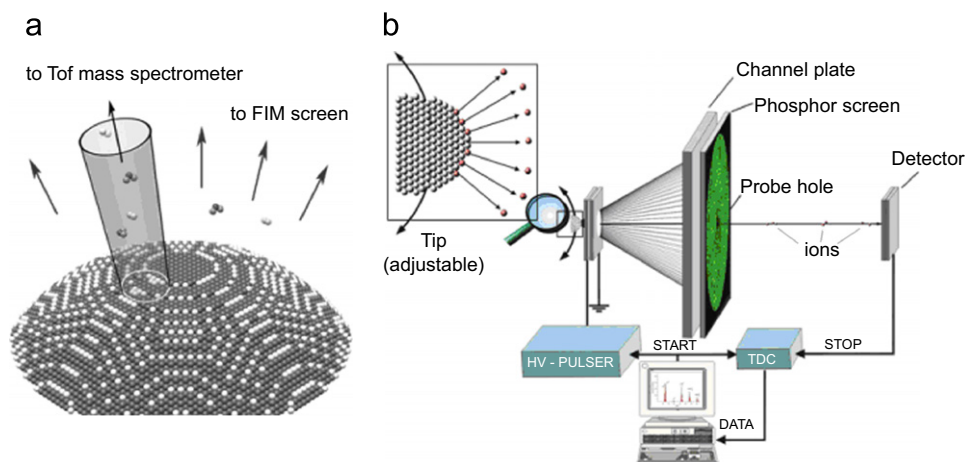


Fig. 1. (a) Basic principle of the atom-probe technique [13] and (b) scheme of the apparatus.

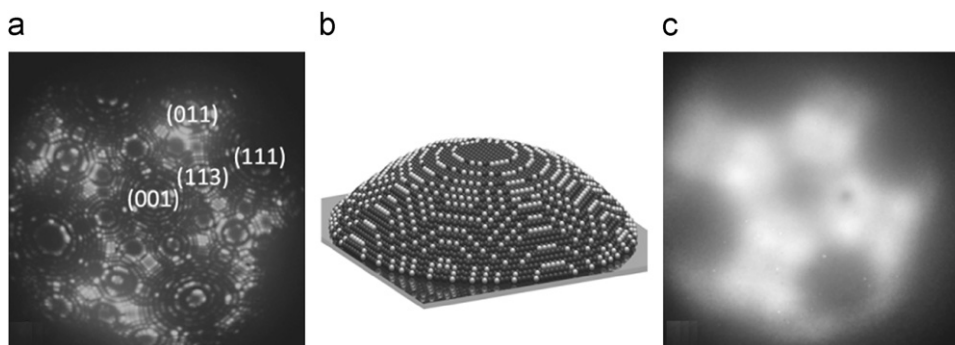


Fig. 2. (a) Neon-field ion micrograph of a (001)-oriented Ni tip; (b) ball model demonstrating the 3D nature of the tip; (c) corresponding FEM micrograph.

was introduced into the microscope chamber through a high precision leak valve. Ethanol experiments were realized by connecting a flask containing high purity  $C_2H_5OH$  and by using its vapor pressure to fill a gas line leading to a high-precision leak valve.

Tips were first characterized by Ne-FIM at 50 K (Fig. 2 shows a typical micrograph of a Ni tip (a) along with a ball model (b) to provide a guide to the eye of the 3D nature of the crystal atomic arrangements). Experiments were then realized by exposing the sample to reactive gases ( $p \leq 10^{-2}$  Pa) during imaging. To avoid field-induced evaporation of the tip at the relatively high temperatures of the reaction studies, we used the FEM mode of the microscope at fields below 3 V/nm to demonstrate reaction—and thermally induced morphological changes of the Ni tip. Fig. 2(c) shows a typical low-temperature FEM pattern corresponding to the tip presented in (a). To image continuously in the presence of reactive gases, video techniques are applied [13].

### 3. Results and discussion

Starting from a clean and characterized Ni crystal (Figs. 2a and b), the temperature is raised from 50 to 873 K in the presence of hydrogen ( $p = 10^{-4}$  Pa) while imaging with video-FEM. In this way the progressive reconstruction into a polyhedral crystal morphology is monitored through the extension of thermodynamically stable {111} and {100} crystal planes. Only few step sites are left in the end-form, which is in agreement with equilibrium thermodynamics [14] (see Fig. 3(a) for the respective FEM pattern). Real carbon nanotubes CVD synthesis protocols generally

involve a heating step of the catalyst to the working temperature under a reducing atmosphere ( $H_2$  or  $NH_3$ ) before introducing the carbon-containing gas. We show here that Ni particles reach a faceted equilibrium shape during this initial treatment.

Directly after this pre-treatment,  $C_2H_2$  was added to the hydrogen atmosphere. This caused another significant morphological transformation as evidenced by video-FEM (see the sequence of snapshots presented in Fig. 3). The reshaping is observed to proceed through a shrinking of the central (001) and the four {111} planes surrounding it. Consequently, step-containing crystal planes like {113}, located between (001) and {111}, extend. The transformation takes 11 s before going to completion. We conclude from this observation that carbon released from the decomposition of  $C_2H_2$  induces the formation of additional step sites. Preferential carbon adsorption in fivefold coordinated Ni step-sites has moreover been calculated recently [9]. The energy requirements of this restructuring are fulfilled by the strong exothermicity of the reaction [15].

Three seconds after completion of the shape transformation, a very bright pattern is observed to quickly invade the whole surface from a hardly distinguishable nucleation point (not shown here). We therefore reproduced the experiment in “softer” conditions (723 K and by replacing  $C_2H_2$  by  $C_2H_5OH$  which is less reactive). This time, the high-brightness pattern nucleated precisely in the step-containing {113} planes (see Fig. 4). As the overall brightness is strongly increasing with time, this observation has to be related to the nucleation and growth of a material which decreases the surface work function. This material could most probably be graphitic carbon [16] which is known to be

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