Synthesis of vertically aligned carbon nanotubes and graphite on stainless steel by chemical vapor deposition

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Carbon-based nanostructures as graphene or nanotubes are currently under intense investigation due to their exceptional combination of electrical, thermal and mechanical properties. Although they can be synthesized by a wide variety of methods, catalytic thermal chemical vapor deposition (CVD) is probably the most promising one due to its high control and scalability [1], [2]. It consists on the high temperature decomposition of a hydrocarbon nearby a substrate, where these nanostructures are synthesized. The election of this substrate is of major importance for the commercial feasibility of CNT-enhanced materials; a low cost and flexible substrate that can be folded inside a CVD reactor will enable to scaling up a continuous synthesis process. Thus, metallic foils have been proposed as catalytic substrates to synthesize graphene sheets of several cm^2 [3] or vertically aligned CNTs forest [4].

In this work we studied the synthesis of vertically aligned carbon nanotubes (VACNTs) and graphite by atmospheric pressure CVD on a stainless steel flexible foil (304 grade). The stainless steel was pretreated by air-oxidation. In order to perform fast heating and cooling ramps, the furnace was mounted on a wheeled mobile platform sat on a pair of rails. The CVD process on the stainless steel consisted on a first reduction step followed by a synthesis step. Both steps were carried out in a tubular furnace at temperatures between 700ºC to 830ºC.

After the CVD process, we have studied the synthesis products. Regarding the VACNTs, two temperature intervals were clearly observed; a low temperature interval where VACNTs of a maximum length of 7 µm are obtained, and a high temperature where a progressive decrease in their length took place. Raman spectra directly collected on substrates after VACNTs removal, indicated the presence of a graphitic carbon layer deposited on its surface. In order to corroborate this result, several samples were etched in acid, and after substrate dissolution, a floating graphite-like layer was observed. TEM micrographs of CNTs and graphite confirmed the presence of both CNT and graphite (Fig. 1).

A study of the stainless steel at different stages of the process was carried out. The XPS spectra showed the effect of the oxidation pretreatment, that was the incorporation of Fe_2O_3 in the original passivation oxide layer of the stainless steel (Cr_2O_3), and the next reduction step, that partially reduced it into metallic Fe. After synthesis at low temperature, the substrate did not substantially change its surface composition. However, at higher temperature a significant increase of carbon incorporation into the substrate was detected. The XRD studies showed phase transitions on its surface (martensite to austenite), and formation of carbides, indicating the sensitization of the stainless steel during the whole treatment. As a final result, microstructural evolution of a cross section is analyzed by SEM, showing an acicular microstructure on the pristine stainless steel and an increase of the grains size after synthesis.

A simple and feasible method to synthesize VACNTs forests and graphite on commercially available stainless steel foil is demonstrated. The oxidation-reduction of the stainless steel prior to the synthesis step was necessary to obtain VACNTs. However, the VACNTs are not present at high synthesis temperature (about 780ºC), where a significant incorporation of carbon into the stainless steel was found, as well as microstructure evolution. Further work needs to be done in order to understand the growth mechanisms involved in such a heterogeneous substrates so high quality and inexpensive VACNTs and their related materials can reach the market.

References

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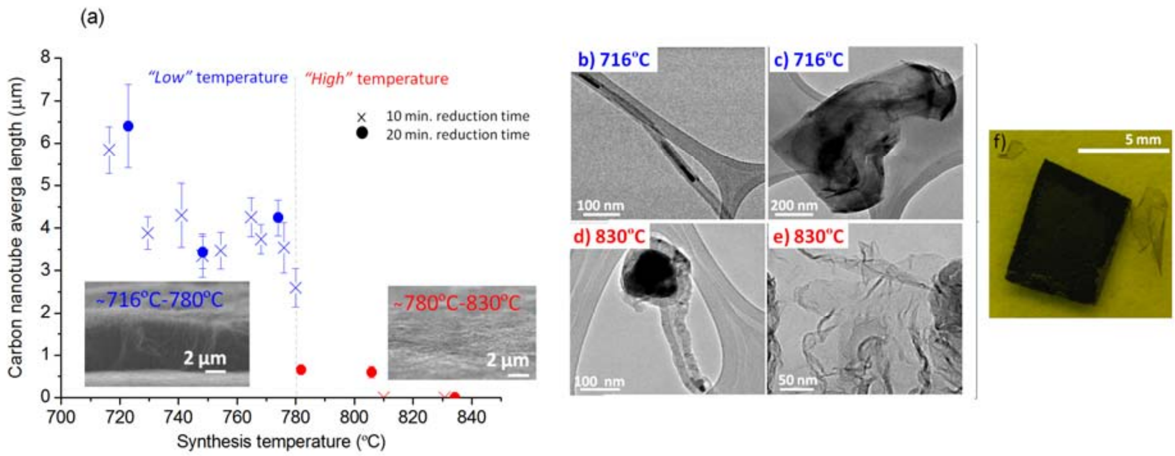

Fig. 1 Influence of the synthesis temperature on the VACNTs length. a) Low synthesis temperature leaded to VACNTs, and high synthesis temperature leaded to no observable CNT by SEM. TEM micrographs indicating a CNT and a graphite flake at b, c) 716ºC and d, e) 830ºC. Graphite layer detachment during stainless steel dissolution in acid.