Carbon nanotubes growth from L-type and AlPO4-5 zeolites by thermal chemical vapour deposition

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The use of Carbon Nanotubes (CNTs) is considered as one of the most promising alternatives for the fabrication of nanoelectronic devices. However, there are two main technological difficulties that need to be solved: control over the chirality of the nanotubes and their placement at desired positions in a determined direction on the substrate.

The first approach for controlling the CNTs structure consists in obtaining narrow distributions in diameter of the nanotubes. For this aim, it is necessary to control the size of the catalyst particle. However, although patterned growth of CNTs can be afforded through Chemical Vapour Deposition (CVD) growth by a selective deposition of catalyst, the nanotube growth direction cannot be controlled in batch synthesis.

Zeolites are crystalline microporous materials that have ordered and oriented pores of less than 2 nm in diameter [1]. These materials are an option for CNTs controlled growth as their pores can be used as a container for catalyst and as a guide for CNT growth.

We have studied growth of CNTs by CVD when placing the catalyst inside L-type (Fig.1 (a)) and AlPO4-5 (Fig.1 (b)) zeolites. The pore diameter is 0.71 nm and 0.73 nm for the L-type and the AlPO4-5 zeolites respectively. Fe/Co was used as catalyst in both types of zeolites. Fe/Co particles, up to 2.5% of the total mass, were introduced in the pores of the L-type zeolites. In the case of AlPO4-5 zeolites, 1% of the atoms forming the structure were substituted by catalyst ones. Zeolites were then dispersed in ethanol and the solution was spin coated on Si substrates. Growth of CNTs was performed in a Rapid Thermal CVD system where temperature ramps up to 30ºC/s can be applied. Process temperature was maintained in each experiment at 800ºC. CH_4 was injected as the carbon containing gas, and H_2 as the supporting gas that activates the formation of the CNTs.

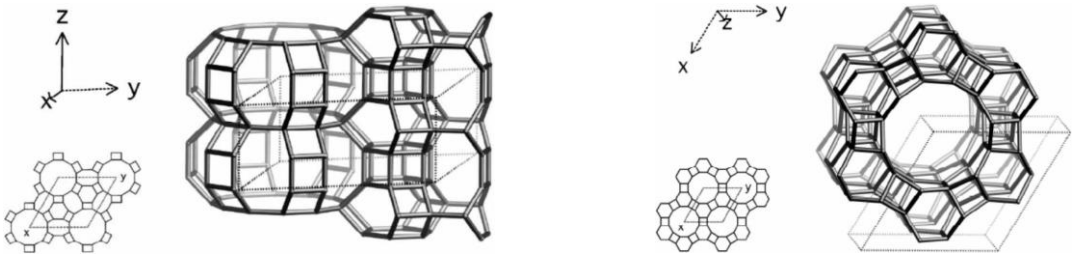
SEM images and Raman spectra in Fig.2 and Fig.3 demonstrate growth of CNTs from L-type and AlPO4-5 zeolites. In the case of L-type zeolites, either small densities of SWCNTs (Fig.2 (a)) or high densities of CNTs (Fig.2 (b)) have been obtained. E-beam etching of the zeolite (inset in Fig.2 (a)) has demonstrated SWCNTs grow from inside the zeolites. In the case of AlPO4-5 zeolites, although there is no SEM evidence of CNTs growth (Fig.3 (a)), Raman spectra (Fig.3 (b)), which is in accordance with ref. [2,3], confirms growth of 0.420 nm and 0.397 nm in diameter SWCNTs.

In conclusion, we have been able to grow SWCNTs in the porous of L-type and AlPO4-5 zeolites, as the first step for the batch synthesis of oriented nanotubes at wafer scale. In parallel, the fabrication of specific surface patterns for selective and oriented deposition of L-type zeolites on the substrate is being examined. When zeolites deposition parameters will be optimized, we will be able to control the location, direction and the density of CNT growth on a substrate.

References:

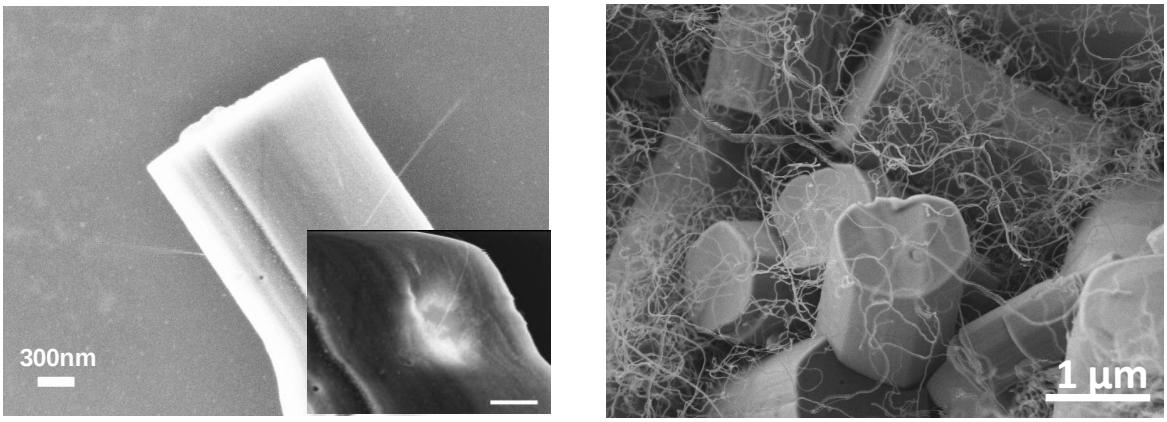
[1] Ch. Baerlocher, W.M. Meier and D.H. Olson, "Atlas of Zeolite Framework Types", 5th ed., Elsevier: Amsterdam, 2001.
[2] Yu, G.J., et al., Diamond and Related Materials, **15** (2006), 1261.
[3] Zhai, J.P., et al., Carbon, **44** (2006), 1151.

Figures:



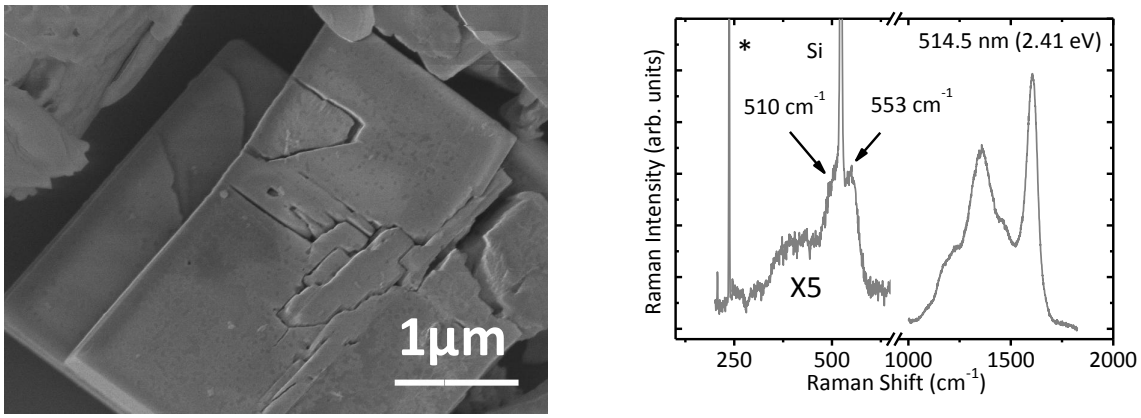
(a) **(b)**

Fig. 1: Frameworks viewed normal to [001] and projection down [001] on the bottom left corner for L type zeolites in (a) and AlPO-5 type zeolites in (b). [1]



(a) **(b)**

Fig.2: SEM images of CNT growth from L-type zeolites. In (a), growth of small density of SWCNTs. An E-beam etching of the zeolite demonstrates CNTs grow from inside the pores. In (b), high density of CNT growth.



(a) **(b)**

Fig.3: SEM image (a) and Raman spectra (b) of AlPO4-5 zeolites after CVD process. Peaks in the Raman spectra at 510 cm^{-1} and 553 cm^{-1} indicate growth of 0.420 nm and 0.397 nm in diameter SWCNTs.