Process conditions influence on carbon nanostructures shaping and self-organizing with respect to the applications

Fabrication at the nanoscale III

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Size, dimensions and shape play important role in determining the properties of nanomaterials, in addition to the chemical bonds. Depending on their relative size in different spatial directions, materials are classified into categories of different dimensionality ranging from 0D (there is no preferential direction for material organization) to 3D (no one dimension is predominant with respect to the others).

Carbon has a unique state of affairs in nature, since it is capable of giving rise to a variety of novel materials such as fullerenes and nanotubes, and well known graphite and diamond. In the carbon system different classes of nanomaterials can be grown: zero-dimensional fullerenes, one –dimensional nanowires/nanofibres/nanotubes, two-dimensional nanowalls [1].

Graphite sheets are unstable and usually tend to curve and roll up in either one or more directions leading to the formation of closed structures (fullerenes, cages, cones and tubes). 2D graphite sheet based materials, such as carbon nanowalls, are less available than those with tubular structure, being characterized by an open boundary. Such materials are obtained when conditions for assembling in a self-supported network are achieved.

Recently we have succeeded in growing several types of nanomaterials in the carbon system, produced by chemical vapour deposition processes, both plasma and hot filament activated.

Carbon NanoFibres, with diameter ranging from 20 to 100 nm, were obtained with a Plasma Enhanced CVD process, starting from a gaseous mixture of CH_4 and H_2 in the ratio of 1:7, on carbon substrates coated by Ni clusters as catalyst. Depending on the alignment of the graphene layers relative to the fiber axis, carbon nanofibres with different types of morphology were observed: "platelet" where graphene planes are aligned perpendicular to the fiber axis and show an ordered structure with the same interlayer distance (see panel a in the figure), "herringbone" which has the graphene alignment angled by 50–70° to the fiber axis, and "tubular" where the graphene sheet is parallel to the fiber axis (see panel b of the figure) [2].

The transition from one type to the other type of fibre was obtained in a controlled process, using the same mono-elemental catalyst and the same precursors gaseous mixture, keeping constant the total pressure and varying the substrate temperature. These materials were characterized by structural and spectroscopic techniques. A relation between the organization mechanism and the dynamic of the growth has been proposed.

Carbon nanowalls were grown on silicon substrates with a Hot Filament assisted CVD process, from a precursor mixture of CH_4 and He. The elemental 2D-structures, with lateral dimension ranging from 10 to 100 nm and thickness lower than 2 nm, were assembled in a homogeneous network perpendicularly to the substrate (see panel d in the figure). The effect of the substrate polarization on the initial growth stage and the film final morphology was

studied. It has been found that a silicon surface modification (induced by an etching in situ pre-treatment under hydrogen atmosphere) is itself a sufficient condition for graphene sheets arranging perpendicularly to the substrate. The application of the external field influenced the following growth stage, determining the nanowall lateral dimension and the film thickness. Moreover the presence of a catalyst was found unessential for the growth, but useful for a patterned coating of the substrate (see panel e in the figure).

Tailoring the morphology at the nanoscale enlarges the field of application of carbon nanomaterials. Here two examples of device components fabrication are reported. A novel reinforcement element for polymeric matrix composites, constituted of carbon nanotubes directly grown onto carbon fibres (see panel c in the figure), has been realized combining the nanoscale properties of carbon nanotubes with the microscale features of traditional carbon fibres [3].
The large surface to volume ratio of two dimensional carbon sheets, that is theoretically twice that of the closed boundary structures, make them very promising for chemical and biosensor applications. In this frame, a novel electrode for fuel cells, where the catalytic layer is made of Pt clusters deposited on carbon nanowalls, has been realized (panel f in the figure). An enhancement of the catalytic activity has been measured compared to traditional electrodes [4].
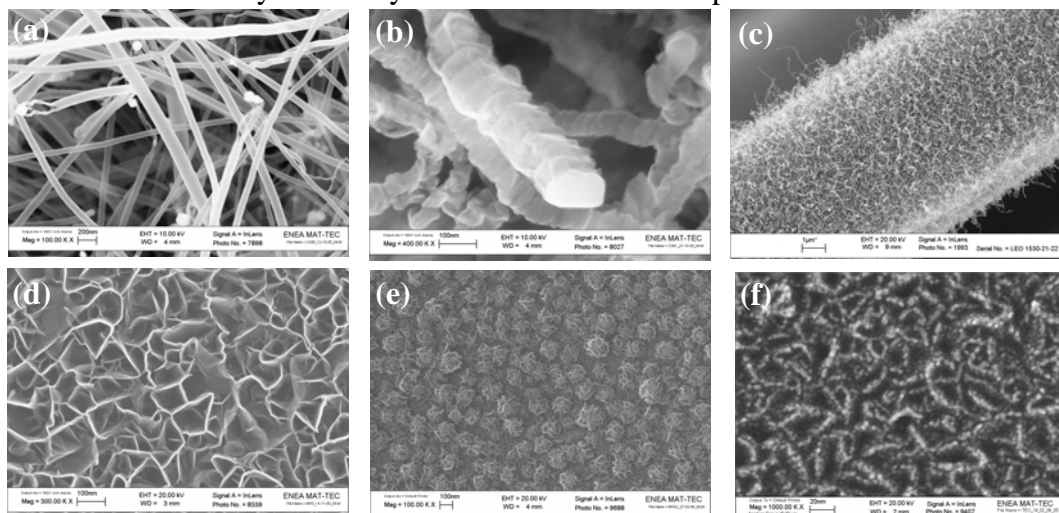

Figure: (a) Carbon nanofibres with tubular and (b) platelet morphology, (c) growth of carbon nanotubes on carbon fibres, (d) growth of carbon nanowalls on silicon substrate without catalyst and (e) using Ni clusters as catalyst, (f) carbon nanowalls as template for Pt clusters deposition for electrochemical applications.

Keywords: Carbon nanostructures, CVD

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