Synthesis of Cobalt nanowires by in-situ Environmental TEM

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1. INTRODUCTION

Owing to their exceptional mechanical, electric, optic and/or magnetic properties, metallic nanowires (NWs) have received in the last years particular attention as promising candidates for diverse applications requiring well-defined designs and properties. There is however a huge drawback related to the controlled synthesis of such structures. Apart from the expensive routes as for example the focused ion beam, the method the most employed makes use of amorphous templates with controlled geometries allowing either the growth or deposition of metals in the pores. Afterwards the template is burned and/or chemically dissolved, such that the nanowires with the desired characteristics are obtained. Since the physical and chemical properties of cobalt (Co) range from high mechanical ductility and interesting electric and magnetic properties to an important catalytic activity, it is one of most employed metals in applications as it exhibits high catalytic activity. The main disadvantage while using 3d metals is their behavior when in contact with the air: they oxidize very quickly and the oxide layer changes drastically their properties. In this context, the question arising is whether Co nanowires can be synthesized in a neutral milieu and further protected against oxidation. To answer this query, we turn to in-situ transmission electron microscopy (TEM) in the high temperature range. The idea is to use Co nanoparticles (NPS) inserted in carbon nanotubes (CNTTs) which will constitute the protective shell. The system is heated in the high temperature range, such that the Co coalesces and NWs form, being protected against oxidation by the CNT. The most pessimistic scenario implies the NWs oxidation at the ends during manipulation. The choice of CNTs as shell is not random as they exhibit exceptional mechanical and electrical properties and they have been successfully tested as well as supports in catalysis.

2. RESULTS

2.1 Experimental methodology

The in situ TEM analyses have been carried out in a Jeol2100F TEM equipped with C_s probe corrector under Scanning TEM (STEM) mode, an EDS detector and an EEL spectrometer. A Gatan heating holder has been used for the heating under vacuum, whilst the environmental experiments have been carried by using the Protochips Atmosphere Environmental Gas cell. It allows performing observations under gas flow or static conditions, for pressures up to 1atm and temperatures up to 950°C, without loosening the microscope performances. The specimen was dispersed in ethanol and then deposited onto the Echips i.e. SiN@SiC windows, which were mounted on the specimen holder. In our experiments we used pure hydrogen as reductive medium and the experiments were carried out at 700 torr and 900°C under continuous gas flow. A pretreatment under Ar at 200°C and 200 torr has been performed in order to remove all the contaminants from the tube and membranes surface.

2.2 Evolution of the catalyst morphology and the active phase distribution

Co oxide crystals with inner fractures have been growth inside multi walls CNTs. Under vacuum, the fractures completely close at 300°C, whereas the particles diffusion starts at 400°C but the presence of residues in the tubes hinders particles sintering. After ex-situ reduction in hydrogen atmosphere, the NPs fractures open such that each NP is constituted by assemblies of smaller NPs, disposed on well-defined geometries i.e. octahedrons, similar to the shape of the non-reduced particles. When submitted to a hydrogen flow at the atmospheric pressure and at 700°C, several types of abrupt microstructural changes are identified, as displayed in the upper row from Figure 2. In the case of a tube partially filled or with small number of particles, the amount of metals is not enough to generate a nanowire and therefore one assists at the increment of NPs size. If the quantity of metal is enough, porous or compact wires form in the tubes, as cumulated effect of NPs reduction and subsequent coalescence. One has to keep in mind that the specimen is placed in a cell and a thickness of 5µm of gas is crossed by the beam. The incident beam ionizes the gas in the cell acting as etching agent for the carbon atoms which are progressively dislodged during irradiation. As consequence the number of CNTs walls until the cobalt wire remains unprotected.

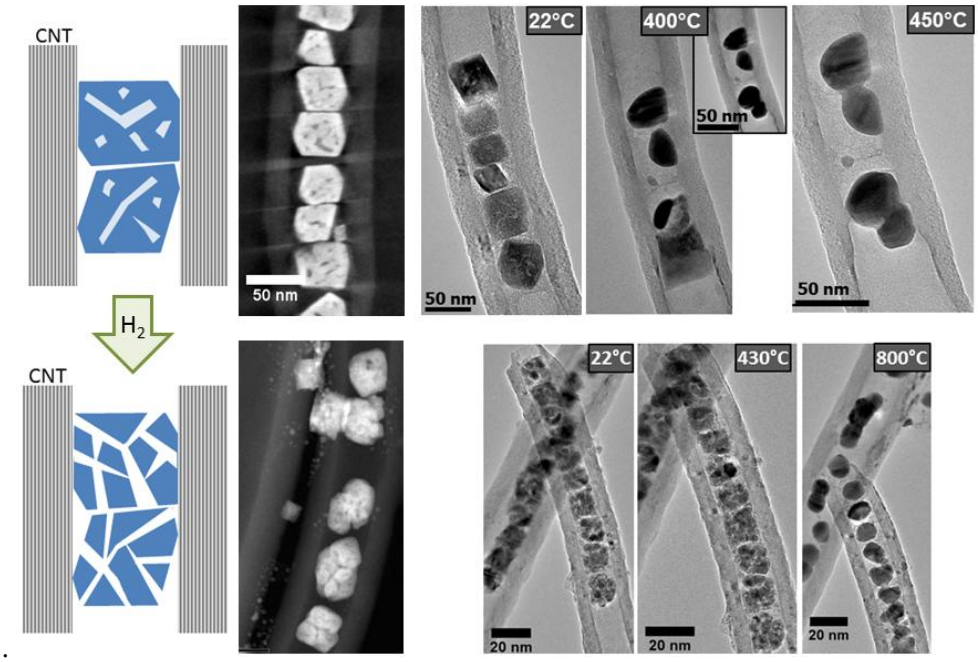

Figure 1. Schematic representation and TEM micrographs of morphology changes as induced by the hydrogen assisted reduction treatment (left side) and in situ thermal treatment under vacuum [1]

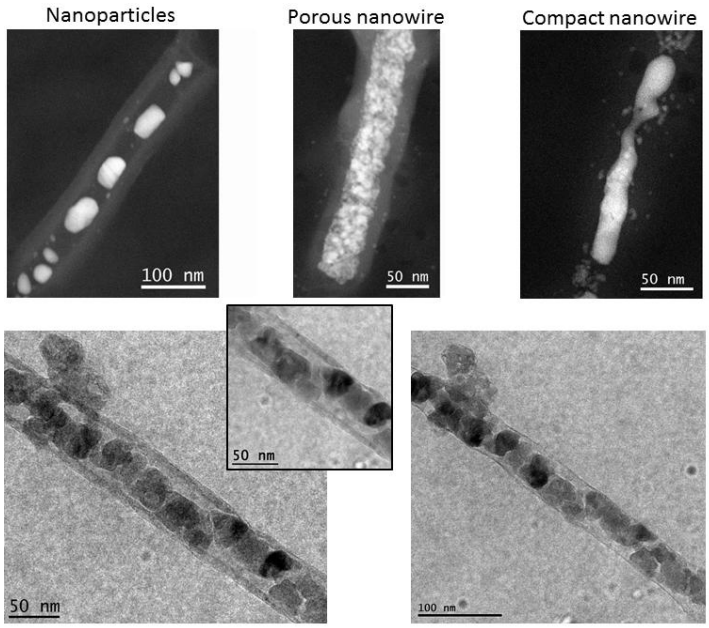

Figure 2. Microstructural changes of the CoO@CNTs induced by the hydrogen flow at 1 atm pressure and 700°C (up). TEM micrographs showing the beam effect on the tube's morphology

3. CONCLUSION

Environmental TEM was used successfully used as method for the in-situ synthesis of Co porous and compact nanowires encapsulated in CNTs. Thermal treatment alone under vacuum carried out on as-prepared and reduced specimens was not enough, a finding that strengthens the importance of the hydrogen atmosphere to generate such structures creation of hydrogen. The role of electron irradiation remains to be elucidate in order to better control the process of synthesis.

REFERENCES

[1] Baaziz W, Florea I., Moldovan S., Papaefthimiou V., Zafeiratos S., Begin-Colin S., Begin D., Ersen O.,, and Pham-Huu C., J. Mat. Chem. A, DOI: 10.1039/c5ta00283d.