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SYNTHESIS AND CHARACTERIZATION OF N-DOPED MWCNT BY CCVD USING A BIPHASIC SUBSTRATE: Ni/$La_2Zr_2O_7$

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Introduction

In the synthesis of carbon nanotubes (CNTs) by catalyst chemical vapor deposition (CCVD) the selection of the catalyst plays an important role. High carbon solubility is the most important request for the catalyst. Transition metals (TM) fulfill such demand. Among the most used TM elements, Ni is widely used because of its suitable catalytic activity and low cost. However, Ni has problems with the sintering and coalescence of the particles that increases its size and decrease its dispersion[1,2]. This leads to the need of a suitable support for Ni nanoparticles. The greater the initial dispersion and the interaction with the support the lower the occurrence of this negative process.

Oxides with abundant oxygen vacancies have been used to promote the dispersion of Ni since this improves the interaction with the support[3]. Lanthanum oxide is a good choice for supporting the Ni nanoparticles because it could enhance the concentration of Ni in the surface[4] and promotes a fast growth rate of carbon sheets from the surface of catalyst particles[5].

The bimetallic oxide $La_2Zr_2O_7$ (LZO) presents additional oxygen mobility by the incorporation of La in the ZrO_2 lattice. This oxide could be an interesting support when it is prepared by a co-precipitation method and calcination over 780 °C[6]. This allows a phase separation process giving a biphasic material, NiO/LZO, with a good dispersion of NiO nanoparticles.

In this work we evaluate LZO as catalyst support for 20 % of Ni to synthesize N-doped multiwall CNTs (N-MWCNTs) by CCVD using benzylamine as carbon and nitrogen source. The incorporation of N could change the electrical properties of CNT and produce new active sites on their surface[7].

Materials and Methods

The catalysts-support were prepared by co-precipitation following the method of Bussi et al[6] using $Ni(NO_3)_2$, $La(NO_3)_3$ and $Zr(OCH_2CH_2CH_3)_4$ (Sigma–Aldrich). The resulting solid was dried at 100 °C for 24 h and calcined at 550 °C for 24 h and finally calcined at 900 °C for 2 h.

The CCVD reactor consists of a quartz tube inside of two horizontal tubular furnaces (BL, Barnstead Thermolyne), placed one after to another. The precursor was benzylamine cloud (Sigma Aldrich) which was transported utilizing a flow of Ar-H_2 (95:5) (2.5 $Lmin^{-1}$) and produced by a nebulizer-sprayer equipment. The synthesis was performed at four different temperatures, 800 °C,

850 °C, 900 °C y 950 °C, during 30 min with a previous reduction for 20 min. The mass of catalyst-support employed was 1g.

The samples were characterized by transmission electron microscopy, HRTEM (Jeol COM 200kV), Raman spectroscopy (WITec, model Alpha 300RA, λ = 532 nm), X-Ray diffraction, DRX (RigakuUltimaIV fitted with CuKalpha) and thermogravimetric analysis, TGA (Shimadzu TGA-50).

Results and Discussion

The HRTEM images shows bamboo-shaped N-MWCNTs. Some parts of the walls showed strains (orange square in figure 1a) and wavy walls. Ni nanoparticles were found inside of the N-MWCNTs (figure 1b). These nanoparticles were dragged during the nanotube's growth.

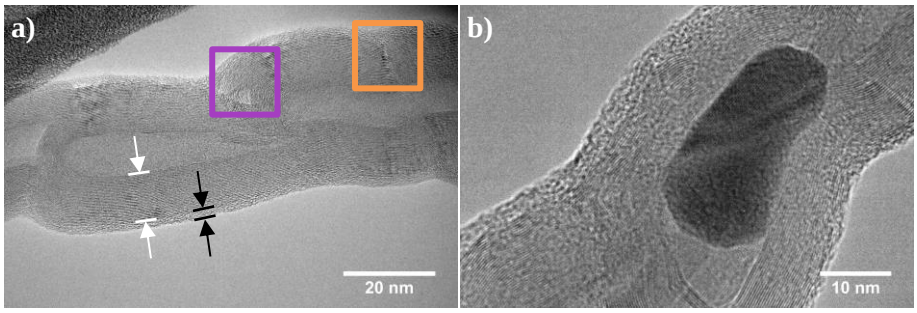

Figure 1. TEM image from sample CNT900, a) a N-MWCNT showing wavy walls, staking defects (violet square), strains (orange square), graphitic-like core (white arrows) and amorphous-like external walls (black arrows), b) a Ni particle inside a N-MWCNT.

In the deconvoluted Raman spectra four bands were identified (figure 2a). The typical G band associated with in-plane tangential stretching C-C bond and D band related to the breathing mode of six-atom rings[8] activated for the presence of defects. The I band that often appears as a broad shoulder to the D-band is related to doping with N. The D** band is associated with staking defects[9].

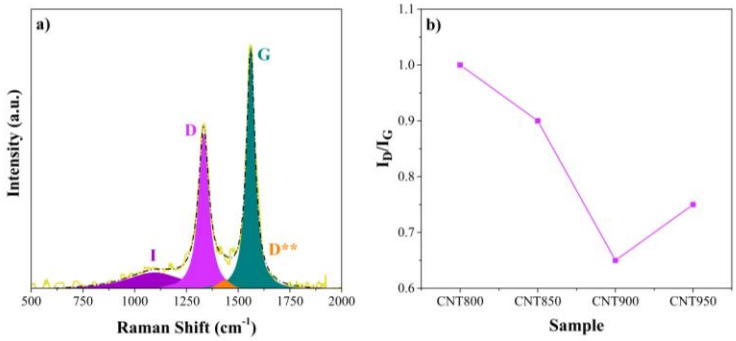

Figure 2. a) Deconvolution of Raman bands for sample CNT900 showing bands I, D, G and D that can be associated with the incorporation of N, sp^2 network defects, C-C stretching and staking imperfections, respectively, b) I_D/I_G ratio vs sample.**

The I_D/I_G ratio decrease with the increase of reaction temperature except for CNT950 (figure 2b). These results demonstrate that the higher reaction temperature contributes to obtain better graphitization degree because of the increasing carbon diffusion rate in the catalyst[10]. The

exception for CNT950 could be due to the calcination temperature that is lower than the reaction temperature used, which could increase the nanotubes growth disorder.

The DRX results confirm the presence of $La_2Zr_2O_7$ and Ni after the CNT synthesis. Ni is the active metal and comes from the reduction of NiO. However, there is a shoulder in the Ni peak and its deconvolution indicate the presence of NiO.

Table 1. TGA results. Temperature for the maximum rate of oxidation (DTG peak) and range of oxidation.

Sample	CNT800	CNT850	CNT900	CNT950
Oxidation.range (°C)	420-654	500-647	450-663	450-663
$T_{max.\ rate\ of\ ox.}$(°C)	537	578	603	543

According to the TGA results, the temperature for the maximum rate of mass loss (DTG peak) increases as the reaction temperature increases, except for CNT950, which is in agreement with Raman results. A higher degree of graphitization implies a more thermally stable material. However, the temperature oxidation ranges are wide and the DTG peak is asymmetric, which means the synthesized N-MWCNTs are non-homogeneous. This could be due to the existence of a more crystalline core and an amorphous-like outer layers, white and black arrow, respectively in figure 1. For CNT950 the derivative shows two peaks evidencing the presence of two different materials that could be associated with two different catalyst structure at high temperature.

Conclusions

The catalyst Ni20/LZO is active for N-MWCNTs growth with bamboo-shaped at 850°C using benzylamine as precursor. The growth dragged Ni particles and increase its dispersion. In the deconvoluted Raman spectra I, D, D** and G peaks were identified and can be associated with the incorporation of N, sp^2 network defects, C-C stretching and staking imperfections, respectively. The I_D/I_G ratio increase with the reaction temperature. This is in agreement with the increment in the DTG peak temperature, because a higher I_D/I_G ratio implies a higher graphitization degree and a more thermally stable material. The CNT950 was an exception and it could be due to a change in crystalline structures of the catalyst-support at high temperatures. Future studies will determine the potential applications of these materials.

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