

Ordered and Disordered Carbon Structures Detected by TEM in Carbide-derived Carbons Produced from TiC

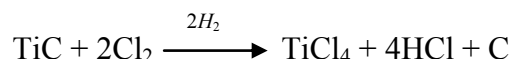
P.G. González¹, E. Urones-Garrote², D. Ávila-Brandé³, L. García-González¹, L.C. Otero-Díaz³

¹. Centro de Investigación en Micro y Nanotecnología, Universidad Veracruzana, 94294, Boca del Río, Veracruz, México.

². Centro Nacional de Microscopía Electrónica, Universidad Complutense, 28040, Madrid, España.

³. Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense, 28040, Madrid, España.

Nowadays, the selective etching of metal carbides by chlorine gas is one well established method to prepare highly porous and nanostructured carbon materials with potential applications for hydrogen storage and supercapacitors. The obtained products usually named as carbide-derived carbons (CDC) present high purity, high surface area and homogeneous pore size distribution and most of times present a graphitic structure; however, in some cases, disordered carbon nanostructures coexist among the ordered ones [1]. In this study, we report the synthesis and characterisation of CDC materials obtained from TiC at 900 °C. Powder precursor, purity of 99% Aldrich, was heated at 50 °C/min in a tubular furnace during 2 h, in a continuous flow of a mixture containing high purity chlorine gas (25 mL/min) and hydrogen (2.5 mL/min) according to the next possible scheme:



TEM studies were performed with a JEOL 3000F (acceleration voltage of 300 kV) microscope (point resolution of 1.7 Å) equipped with an ENFINA spectrometer for EELS measurements. Two types of CDC particles were detected during the TEM studies. The contrast observed in the High Resolution TEM image of Figure 1a is characteristic of a highly disordered carbon material formed by wavy graphene-like layers. This kind of nanostructure has been frequently reported as the main structure of the CDC [2,3]. In contrast, Figure 1b shows a CDC particle with a graphite-like ordered structure containing a high amount of graphitic domains. These structural differences can be confirmed looking at their corresponding DDP patterns. Presence of diffuse diffraction rings in the DDP of Figure 1a is typical for disordered materials. On the other hand, the graphitic structure is demonstrated by the DDP of Figure 1b which can be indexed along the [0-10] zone axis.

The ELNES of the carbon K adsorption edges from both particles present the characteristic π^* and σ^* peaks. The round and featureless σ^* peak in Figure 1c is also an evidence of the disordered nature in the graphenic-like CDC. On the other hand, a well defined and sharp σ^* peak (Figure 1d) is indicative of a high graphitization degree in the structure of the ordered CDC. From these observations is possible to say that two type of carbon (ordered and disordered), coexist as main structure of this CDC. Finally, the relative sp^2 content was calculated from the ratio of the integrated intensities provided by the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transition peaks according to the two-windows centrally positioned method [2]. Results show a sp^2/sp^3 bonding ratio of 82 and 100 % respectively, in agreement with the nanostructure detected by HRTEM and EELS.

References:

- [1] V. Presser, M. heon and Y. Gogotsi, *Adv. Funct. Mater.* **21** (2011), p. 810.
 [2] S. Urbonaite, J.M. Juárez-Galán, and F. Rodríguez-Reinoso, *Mic. Mes. Mater.* **113** (2008) p. 14.
 [3] P. González-García, E. Urones-Garrote and D. Ávila-Brande, *Carbon* **48** (2010) p. 3667.
 [4] Acknowledgments: To the projects with references S-2009/PPQ-1626, MAT2010-19460 and CONACYT-154516. P.G. González wishes to thank CONACYT (Mexico) for a postdoctoral grant.

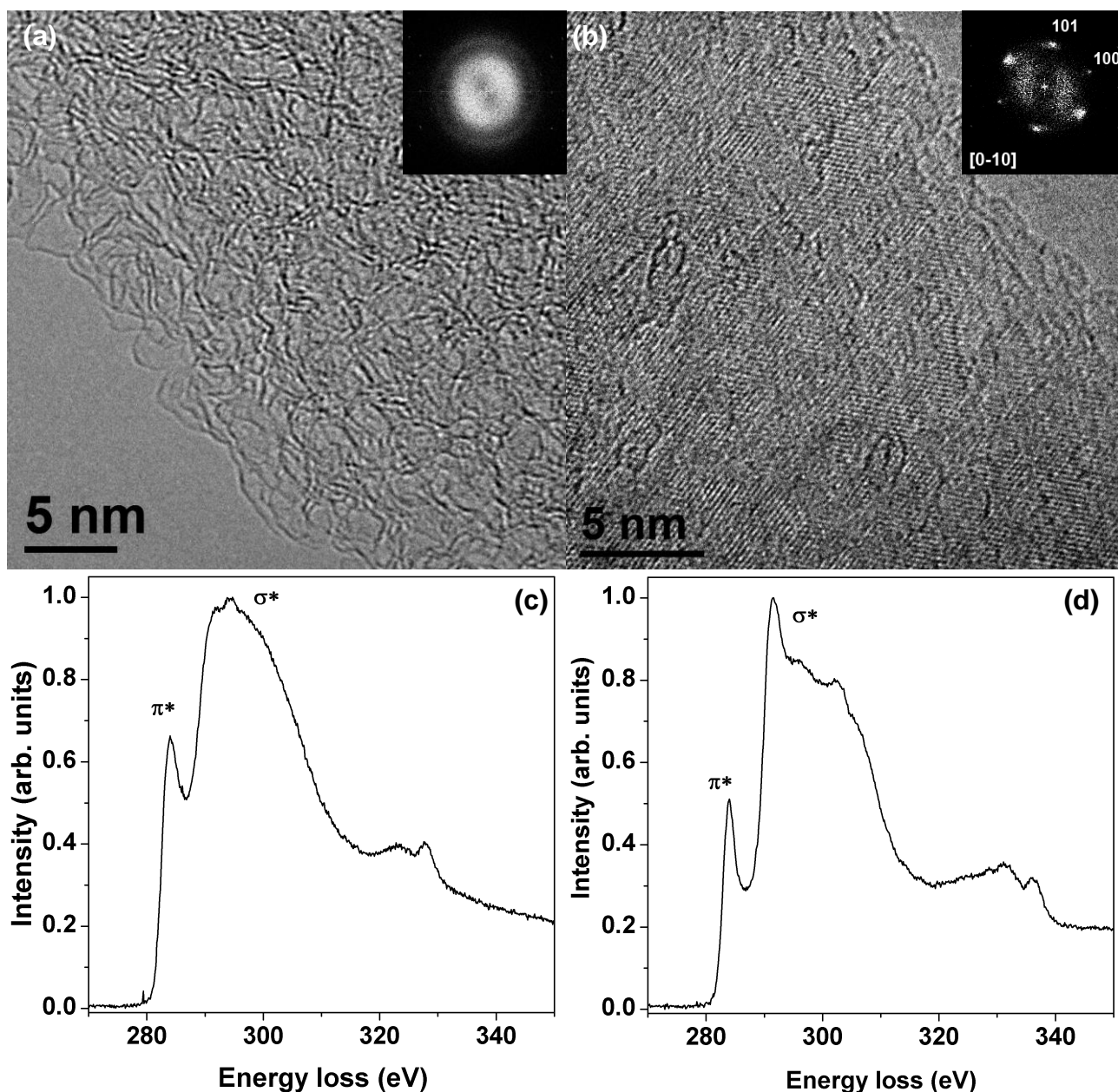


Figure 1. HRTEM images showing CDC particles with (a) disordered graphene-like and (b) ordered graphitic-like structure, as confirmed with their respective DDP (inset). The ELNES having a featureless (c) and sharp (d) σ^* peak also indicate the structural differences of this material.