Carbon nanostructures produced by chlorination reaction of Cr(C₅H₅)₂ and Ni(C₅H₅)₂

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Shaped carbon nanomaterials (SCNM) have reached high importance due to their nanostructural characteristics yielding advance materials for high gas storage capacity and high efficiency supercapacitors [1]. One well established method to produce carbon nanomaterials is the chlorination of metal carbides [2]. In the last years this method has been extended to metallocenes, such as ferrocene [3], as precursors of several carbon nanostructures. In this work, we present the synthesis and characterization of SCNM produced by chlorination of Cr(C₅H₅)₂ (chromocene) and Ni(C₅H₅)₂ (nickelocene). The precursors, powder purity of 97%, were heated in a quartz boat placed in a tubular furnace at 900 °C (heating rate of 50 °C/min) during 30 min, in a continuous flow of high purity chlorine gas (25 mL/min) following the next possible reaction:

\[ M(C_5H_5)_2(s) + nCl_2(g) \rightarrow 10C(s) + MCln(g) + 10HCl(g) \quad (M = Cr, Ni) \]

SEM micrographs, obtained with a JSM 6335 F at 10 kV and a working distance of 15 mm, show the variable morphology of the samples composed by spheres and tubes (Fig. 1a) obtained from chromocene and spheres (Fig 1b) and desert rose–like particles (Fig 1c) from nickelocene. TEM images were recorded with a JEOL 3000 F microscope (acceleration voltage of 300 kV) equipped with an ENFINA spectrometer. For the sample produced from chromocene, the low magnification TEM presented in Figure 2a shows hollow spheres (diameter from 125 to 350 nm and wall thickness from 40 to 55 nm). As it can be observed, the hollow spheres are in cases accreted. Additionally, some thin amorphous carbon tubes (α-CNT) diameter from 60 to 180 nm, length up to 2 µm and wall thickness from 10 to 40 nm, (Fig. 2b) were also found in the sample. By using nickelocene as precursor, we have found corrugated carbon foils (Fig. 2c) and groups of hollow spheres (diameter from 85 to 240 nm and wall thickness from 6 to 40 nm) welded to solid spheres (diameter from 85 to 240 nm) as can be observed in Figure 2d.

After the scrutiny of the HRTEM images/diffracton we notice that these particles are formed by highly disordered graphene layers (see insets in Fig 2), confirmed by the presence of the \( hk0 \)-type reflections in the SAED patterns (see insets). Quantification of \( sp^2/sp^3 \) ratio, obtained by EELS, indicates a high amount of \( sp^2 \) bonding (in the range of 89 – 100 %); the featureless shape of the carbon K adsorption edges follows the characteristic \( \pi^* \) and \( \sigma^* \) peaks of disordered carbon materials. Mass-density obtained from the low-loss region of the EEL spectra, varies from 1.1 to 1.8 ± 0.1 g/cm³ (almost 50% below graphite density = 2.2 g/cm³). The calculated in–plane correlation length of the graphene–like layers from these particles, obtained by Raman spectroscopy, is 1.2 ± 0.1 nm, however the full width half medium value of the particles produced from nickelocene is smaller than the obtained for the chromocene sample, suggesting a higher disorder in the last ones. Finally, the textural data show surface areas from 694 – 726 m²/g and mean pore width around 1.1 nm.

References

Figure 1. SEM micrographs of the SCNM obtained at 900 °C. Tubes and spheres from chromocene (a), beds of spheres (b) and desert rose–like from nickelocene (c).

Figure 2. Low magnification TEM images showing some solid and hollow spheres (a) and a single α-CNT (b) present in the sample produced from chromocene. Corrugated carbon foils (c) and groups of hollow and solid spheres (d) were obtained from nickelocene. Their respective HRTEM and SAED (insets) are indicative of their highly disordered nanostructure.

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