

Reseña Tesis Doctoral. Carbon nanofilaments from catalytic decomposition of methane-rich streams as precursors of graphenic materials.

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OBJECTIVES AND NOVELTY

The catalytic decomposition of methane-rich streams such as natural gas or biogas is a viable alternative to conventional H_2 or syngas production processes such as steam or dry methane reforming. The formation of nanosized carbon materials as carbon nanofibers (CNF) or nanotubes (CNT) plays an important role in the economic feasibility of these processes. This Thesis work addresses the control of the morphology of the carbonaceous products obtained from catalytic decomposition of methane (CDM) and biogas (CDB) by catalysts design, and their transformation into graphene oxide-based materials through oxidation/exfoliation routes.

Thus, Ni and Fe-based catalysts were developed and used for fishbone-like CNF and multi-wall carbon nanotubes (MWCNT) obtention, respectively. The subsequent transformation of these nanofilaments to graphene oxide-based materials was based on its chemical oxidation using the modified Hummers method and subsequent exfoliation by sonication. Resulting graphene materials with different chemical and morphological characteristics included: few-layer graphene oxide (FLGO) from both carbon nanofilaments types, and graphene oxide nanofibers (GONF) and graphene oxide quantum dots (GOQD) exclusively from CNF. The oxygen content of these materials was partially removed by hydrothermal reduction methods, resulting in the restoration of the graphene network. Furthermore, a novel and green reduction method based on the supercritical water

gasification of glycerol was developed, enhancing the reduction performance thanks to H_2 and autogenous pressure generated.

On the other hand, an effective separation process based on degressive differential centrifugation was implemented for the separation by size and oxidation degree of the different fractions obtained by exfoliation of CNF: GONF, FLGO sheets and GOQD. This method produces GOQD in high weight yields with controllable photoluminescent properties by hydrothermal reduction treatments.

Figure 1 summarizes the graphene oxide- and reduced graphene oxide-based materials and oxidation/exfoliation routes of both types of nanofilaments addressed in this Thesis.

RESULTS

Carbon Nanotube Obtention and Derived Graphene-Based Materials

MWCNT were obtained by CDM using Fe and Fe-Mo massive catalysts with Al_2O_3 or MgO as textural promoter. These catalysts were developed and tested in thermobalance determining their optimum formulation, including the effect of Mo doping, and their optimum operating temperature range. The scaling-up was carried out in semi-pilot installations based on rotary and fluidized bed reactors using massive Fe-based catalysts. The behavior of the catalysts in thermobalance was reproduced on this scale, reaching carbon yields of $0.53 \text{ g}_C \text{ g}_{cat}^{-1} \text{ h}^{-1}$ for FeMo/ Al_2O_3 at 750 °C in the rotary bed reactor,

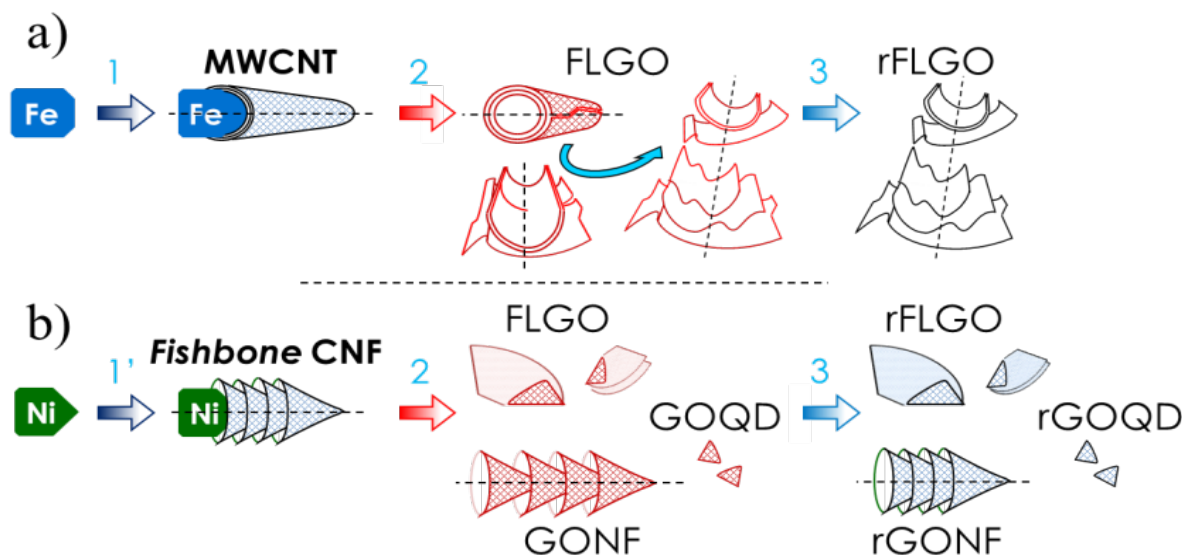


Figure 1. Graphene oxide- and reduced graphene oxide-based materials obtained after (2) oxidation/exfoliation and subsequent (3) hydrothermal reduction, respectively, of a) MWCNT grown from Fe catalysts by (1) CDM and b) fishbone-type CNF grown from Ni catalysts by (1') CDB.

and 0.60 to 0.80 $\text{g}_C \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ for $\text{Fe}/\text{Al}_2\text{O}_3$ at 800 °C in the fluidized bed reactor. Regarding the carbon nanofilaments characterization, the use of Fe and FeMo catalysts mainly promoted the formation of straight and bamboo (discontinuous hollow core) type MWCNT (see Figure 2a-b), with high degree of graphitization and specific surface areas around 70120 $\text{m}^2 \text{g}^{-1}$. Fragmentation of the active metal particles takes place during the CDM resulting in bamboo type structures and the deactivation of the catalyst by encapsulation. Regarding the scaling effect, no significant differences was observed in the characteristics of carbon nanotubes produced. Textural promoters and Fe/Mo ratio had an influence on morphology and diameter distribution of the carbon nanofilaments: higher Fe/Mo ratio resulted in narrower carbon nanotubes.

Homogeneous dispersions of FLGO with a high edge/basal planes ratio were obtained by oxidation/exfoliation of unpurified MWCNT. Characterization of the materials produced with different oxidation degrees clearly showed the surface functional groups evolution during oxidation and structural and morphological changes. The stepwise process of oxidation and exfoliation of graphene layers from MWCNT was found to proceed via the formation of phenol and ether groups, with the subsequent opening of the outer walls and the formation of carbonyl groups. Subsequent exfoliation of graphene planes resulted in the exposure of new planes to further oxidation. In Figure 2c, a partially opened MWCNT can be observed. The full opening of the MWCNT resulted in FLGO sheets (see Figure 2d) from a $\text{KMnO}_4/\text{MWCNT}$ ratio of 6. Higher oxidation ratio resulted in the shortening in size of these fragments. On the other hand, larger diameter nanotubes were easier to open completely than the narrower ones due to the higher defects content, including oxygen-containing functionalities and structural defects, which disrupt the sp^2 -carbon network of exposed graphene layers. On the contrary, narrower nanotubes ($\text{Ø} = 8.6 \pm 3.3$ nm) were more graphitic and straighter than larger ones ($\text{Ø} = 17.7 \pm 11.9$ nm), and led to FLGO sheets presenting non-oxidized graphite stacking, lower

specific surface area and higher thermostability.

A green and efficient hydrothermal method based on the supercritical water gasification of glycerol was developed to reduce FLGO sheets. In this manner, reduction of FLGO and valorization of glycerol was jointly achieved, obtaining at 400 °C rFLGO (see Figure 2e) with a C/O ratio of 29.1, well above those of the traditionally hazardous hydrazine-based methods (C/O $\sim 10.311.5$). It was demonstrated that the sp^2 conjugated graphene network was restored through the removal of basal oxygenated groups. In addition, H_2 , CH_4 , CO_2 and CO gases and valuable liquids products were recovered. The H_2 produced by glycerol gasification enhanced the FLGO reduction in supercritical water, achieving larger oxygen removal than the recently reported process of reduction by water or fluids in supercritical conditions.

Carbon Nanofiber Obtention and Derived Graphene-Based Materials

Fishbone CNF (see Figure 3a) were obtained by DCB using a $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst. As a result of the oxidation/exfoliation process (as shown in the Figure 1b), GONF (Figure 3b), FLGO sheets (Figure 3c) and GOQD (Figure 3d-e) were obtained and successfully separated by degressive differential centrifugation. Decreasing velocities minimizes the entrainment of the small particles along with the larger ones, maximizing the weight yield of the complete centrifugation process. A fraction with a yield as high as 42 wt. % led to photoluminescence response, including GOQD or GObased fractions with active sp^2 domains. Isolated GOQD showed an excitation-dependent photoluminescent emission with a maximum at 578 nm (yellow) for an excitation of 455 nm. Hydrothermal reduction blue shifted the photoluminescence response to the violet light region (448 nm at an excitation of 330 nm) after partial removal of hydroxyl and epoxide groups from basal planes and recovering of graphene network. The photoluminescence quantum yield was dependent on the size and the oxidation state, being the maxima at 5.5 and 7.0 % for GOQD and rGOQD, respectively, in supernatants at 14800 rpm.

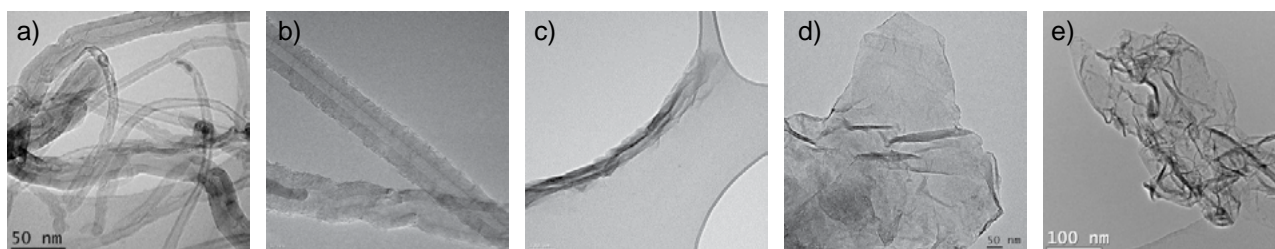


Figure 2. TEM images of a-b) MWCNT, c) partially-exfoliated MWCNT, d) FLGO and e) rFLGO.

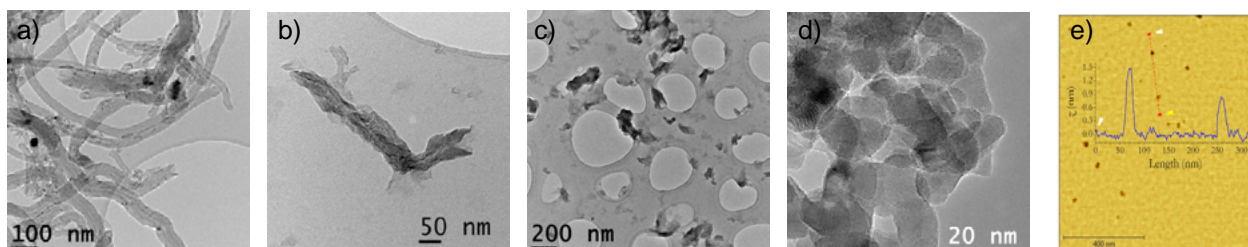


Figure 3. TEM images of a) Fishbone CNF, b) GONF, c) FLGO, d) GOQD; e) AFM image and height profile of GOQD.

CONCLUSIONS

The obtained carbon nanofilaments from catalytic decomposition of methane-rich streams can be used as precursors of graphene-based materials which extends the range of their potential applications. The research work developed along this Thesis shows a comprehensive study of the overall nanostructured carbon materials obtention and characterization as a complementing value in the economic viability of H₂ or syngas production processes.

RELATED PUBLICATIONS

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[⁸] Torres D, Arcelus-Arrillaga P, Millan M, Pinilla JL, Suelves I, Green and enhanced reduction of graphene oxide by supercritical water gasification of glycerol, *Green Chem*, under review.

Full Thesis can be downloaded from

<http://digital.csic.es/handle/10261/142668>