CARBON 2019
LEXINGTON, KY

Well performance production of nitrogen-doped multiwall carbon nanotubes using Fe-rich Leptosol from Sierra de Álvarez, San Luis Potosí, México.

Felipe de Jesús Barraza-García[3], Nadia. Martinez-Villegas[3], Florentino López-Urías[1], and Emilio Muñoz-Sandoval[1,2]*

[1] División de Materiales Avanzados, IPICYT, Camino a la Presa San José 2055, Col Lomas 4a sección, San Luis Potosí S.L.P., 78216, México
[2] Department of Chemical Engineering, Natural and Exact Sciences Division, University of Guanajuato. Noria Alta S/N, Guanajuato, Guanajuato, México 360503
[3] División de Geociencias Aplicadas, IPICYT, Camino a la Presa San José 2055, Col Lomas 4a sección, San Luis Potosí S.L.P., 78216, México

*Presenting author's e-mail: felipe.barraza@ipicyt.edu.mx

Introduction

Endless applications have arisen from carbon nanotubes (CNT) since its discovery in 1991 [1]. Several methods of production of these nanoparticles have emerged, however, the best and most viable methodology to manufacture large amounts CNT and at low manufacturing cost has not been published. [2] One of the fundamental elements involved in the synthesis of CNT using any technique is the catalyst.[3] Commonly, Fe-based nanoparticles (Ni or Co) are used as a catalyst to produce tubular carbon nanomaterials.[4] Despite the difficulty of obtaining clean and good quality CNTs using natural or waste sources, the research to produce carbon nanomaterials from these low-cost materials has become an important field in the carbon area [5]. Su et al. [6] contributed with a large number of natural catalyst alternatives over the years, coming from volcanic rocks, magnesite, bentonite, forsterite, quartz, brucite, and even Croatian red soil. In addition, the use of this type of material allows the development of new strategies to convert very low-cost resources to the industrial quantity of carbon nanomaterials [7]. In this work, we report the use of a red Leptosol rich in Fe as an alternative substrate capable of providing catalytic metal cations in the synthesis of CNT through the CVD technique.

Materials and Methods

The pristine catalyst material used to the present work comes from Sierra de Álvarez, San Luis Potosí, in the central-northern region of Mexico and consists of a red Leptosol rich in Fe. The pristine sample was named as "Soil" and characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA).
Figure 1 shows the process followed to obtain the carbon nanomaterial. The Leptosol is a reddish material (Figure 1a). Ten grams of soil powders were ball milled using an agate vial together with three agate balls. This procedure was carried out to grind the Leptosol powder for 1 hour (Figure 1b). The Leptosol powder obtained was designated 1H (figure 1c). Subsequently, the obtained bad milled powder was placed inside a reactor in an aerosol assisted chemical catalytic vapor deposition (AACCVD) (Figure 1e). This powder was exposed to a reduction process for 20

minutes at 850 ° C using a mixture flow of gases of Ar and H_2 (INFRA) at 2.5 l / min. The precursor solution of carbon and nitrogen consisted of benzylamine (Sigma Aldrich xx% pure). The flow of H_2-Ar (5% -95%) carried the nebulized precursor solution for 40 minutes. Additionally, 1H was subjected to oxidative treatment (labeled as 1H-Ox) to improve the catalytic efficiency of this sample.

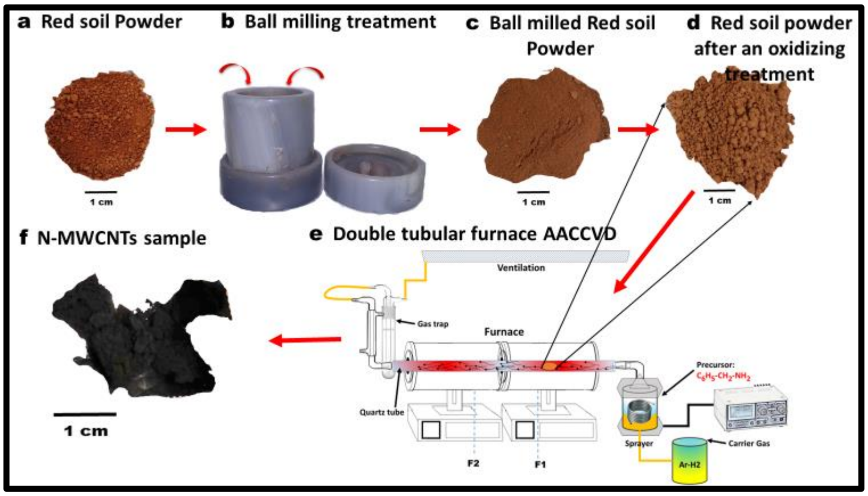

Figure 1. Schematic representation of the steps followed for the production of N-MWCNTs using a Leptosol enriched in Fe as catalysts. (a) Pristine soil, (b) Mechanical grinding treatment, (c) Soil after milling, (d) soil after oxidation treatment, (e) AACCVD system, (f) N-MWCNT.

Results and Discussion

The characterization of the powder of Leptosol through FRX as well as DRX showed the presence of metal oxides, mainly iron and the presence of kaolinite. The Raman spectra of 1H show no significant peaks due to fluorescence from the organic matter contained in the soil. However, after the oxidation treatment, the Raman spectrum shows peaks of iron oxides in the sample.

In synthetized N-MWCNT from sample 1H, we obtained a yield of 76.49%. In the case of using H1-ox the yield of N-MWCNT 98.72%. For the synthesis from the 1H sample, we observed the growth of carbon nanotubes on the leptosol particles (Figure 2a), while for the synthesis from the 1H-Ox sample (Figure 2b) a composed material was created between the leptosol particles and the carbon nanotubes.

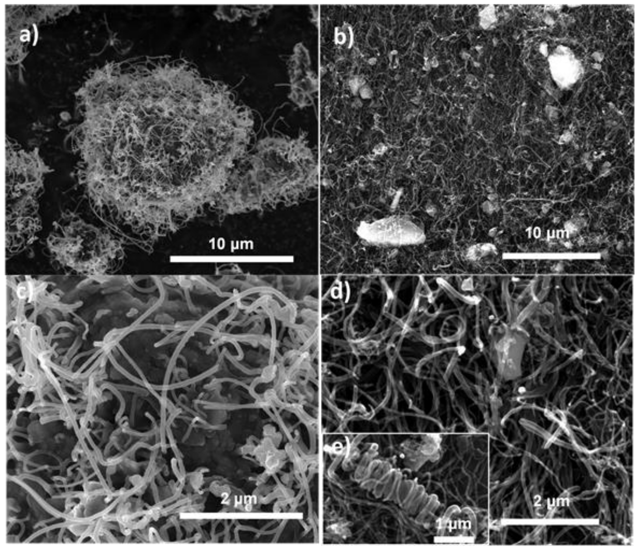

Figure 2. SEM images of the samples synthesized from samples 1H (a, c) and 1H-Ox (b, d) at 5,000X and 25,000X.

Conclusions

We have shown that Fe-rich Leptosol powders can be an effective catalyst for the production of N-MWCNT. It is necessary to emphasize that Leptosol powder is a material with great potential for mass production of carbon nanotubes. Leptosol is an abundant material of low cost, offering an alternative for the production of new carbon materials.

Acknowledgment

FJBG thanks CONACYT for the scholarship from CONACYT. EMS thanks the CONACYT-grant CB-2013-220744, FLU thanks the National Problems project (2016-1-4148-CONACYT). We thank LINAN and IPICYT for the facilities for the characterizations. Finally, we thank M.C. Beatriz A. Rivera-Escoto and M.C. Ana Iris Peña-Maldonado for technical support.

References

1 Iijima, S. (1991) Helical Microtubules of Graphitic Carbon. *Nature*, **354**, 56–58. https://doi.org/10.1038/354056a0.
2 Vivekanandhan, S., Schreiber, M., Muthuramkumar, S., Misra, M. and Mohanty, A.K. (2017) Carbon Nanotubes from Renewable Feedstocks: A Move toward Sustainable Nanofabrication. *Journal of Applied Polymer Science*, **134**. https://doi.org/10.1002/app.44255.
3 Shah, K.A. and Tali, B.A. (2016) Synthesis of Carbon Nanotubes by Catalytic Chemical Vapour Deposition: A Review on Carbon Sources, Catalysts and Substrates. *Materials Science in Semiconductor Processing*, **41**, 67–82. https://doi.org/10.1016/j.mssp.2015.08.013.
4 Harutyunyan, A.R. (2009) The Catalyst for Growing Single-Walled Carbon Nanotubes by Catalytic Chemical Vapor Deposition Method. *Journal of Nanoscience and Nanotechnology*, **9**, 2480–2495. https://doi.org/10.1166/jnn.2009.1297.
5 Titirici, M.-M., White, R.J., Brun, N., Budarin, V.L., Su, D.S., del Monte, F., Clark, J.H. and MacLachlan, M.J. (2015) Sustainable Carbon Materials. *Chemical Society Reviews*, **44**, 250–290. https://doi.org/10.1039/C4CS00232F.
6 Su, D.S. (2009) The Use of Natural Materials in Nanocarbon Synthesis. *ChemSusChem*, **2**, 1009–1020. https://doi.org/10.1002/cssc.200900046.
7 Rinaldi, A., Zhang, J., Mizera, J., Girgsdies, F., Wang, N., Hamid, S.B.A., Schlögl, R. and Su, D.S. (2008) Facile Synthesis of Carbon Nanotube/Natural Bentonite Composites as a Stable Catalyst for Styrene Synthesis. *Chemical Communications*, 6528. https://doi.org/10.1039/b815335c.