

Preparation of carbon nanotubes from plastic solid wastes over magnetic nickel ferrite catalysts

MARIM LOPES J.^{1,2}, ROMAN F.F.^{1,3}, SANTOS SILVA A.^{1,3}, DIAZ DE TUESTA J.L.^{1,*}, LENZI G.G.², SILVA A.M.T.³, FARIA J.L.³, and GOMES H.T.¹

¹Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança

²Universidade Tecnológica Federal do Paraná (UTFPR), Campus de Ponta Grossa, Rua Doutor Washington Subtil Chueire, 330 - Jardim Carvalho, 84017-220 Ponta Grossa PR, Brazil

³Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

*corresponding author:

e-mail: jl.diazdetuesta@ipb.pt

Abstract. This work presents the development of magnetic carbon nanotubes (MCNTs) from plastic solid waste (PSW). For this purpose, diverse catalytic nanoparticles based on Fe, Ni and Al were prepared by impregnation of alumina or co-precipitation of Ni, Fe and Al nitrate salts with NH₄OH, followed by calcination at 800 °C. These magnetic nanoparticles were then used as catalysts in the growth of carbon nanotubes by chemical vapour deposition in a tubular furnace using low-density polyethylene as carbon precursor and as representative polymer composing PSW. MCNTs were characterized by transmission electron microscopy (TEM) and X-ray diffraction. The morphology and dimensions of the MCNTs were observed by TEM, concluding that large multiwalled MCNTs were prepared with magnetic nanoparticles inside (spacing of ~0.2 nm) and with a carbon interlayer spacing of ~0.34 nm. In conclusion, the synthesis of MCNTs from polyolefins is evidenced and can lead to technological alternatives in the treatment of PSWs.

Keywords: plastic solid waste, chemical vapour deposition, nanostructured carbons, magnetic nanoparticles, valorization.

1. Introduction

In 2019, Europe contributed with 15.7% (57.9 Mton) of the plastics (thermoplastics and polyurethanes) produced in the world and demanded 50.7 Mton, of which near 36.8% was polypropylene (PP) and light and heavy density polyethylene (LDPE and HDPE, respectively). Packaging is the main application of these plastics, so typically they have one-single use and are then discarded. In 2019, 29.1 Mton of post-consumer plastic solid wastes (PSWs) ended up in the official waste streams (57.3% of the demanded quantity): 71.5% was recovered through recycling and energy recovery processes. The remaining 24.9% went to landfill (PlasticsEurope 2021). This fact, coupled with the plastic waste long-life, puts in evidence the need to adopt new strategies in order to decrease the

disposal of PSWs and to achieve the objectives of the Directive 2008/98/CE and the principles of a circular economy.

It is evident that plastics bring many societal benefits and offer future technological and medical advances. However, concerns about usage and disposal are diverse and include accumulation of PSWs in landfills and in natural habitats, physical problems for wildlife resulting from ingestion or entanglement in plastic, the leaching of chemicals from plastic products and the potential for plastics to transfer chemicals to wildlife and humans (Thompson et al. 2009). Incineration or recycling are the most common proposed solutions to handle the produced PSW, but incineration contributes to air pollution (J. Aguado et al. 2008) and recycling is not viable in the case of mixed plastic products. Additionally, both processes are costly and may or may not be economically viable in different situations (Passamonti and Sedran 2012).

More attractive strategies are the production of carbon nanomaterials, such as carbon nanotubes and graphene, using PSWs as carbon precursors (Bazargan and McKay 2012; Wen et al. 2015; Zhuo and Levendis 2014). The technology consists in the cracking of the PSWs and further synthesis of the carbon nanostructured materials, using the resultant degradation gaseous products, by catalytic chemical vapour deposition (CCVD). The process requires the cracking of the PSWs, and also the carbonization of degradation fractions. Up to now, most of the publications in this field have studied the production of carbon nanotubes (CNTs) in one step (pyrolysis and carbonization) from a mixture of a pure single polymer with a catalyst (Aboul-Enein et al. 2018; Cai et al. 2021; Jia et al. 2020; Liu et al. 2018; Panahi et al. 2019)

The properties of the CNTs could be finely tuned for specific applications, as demonstrated in a previous work (Diaz de Tuesta et al. 2019) related to the development of magnetic carbon nanotubes (MCNTs) prepared by CVD on magnetic substrates.

This work aims at the development of MCNTs from PSW, using LDPE as representative polymer present in PSWs. For this purpose, LDPE is thermally decomposed and the cracking products carried to substrates based on Fe, Ni and Al, where carbon nanotubes are grown by CVD at 800 °C in only one unit operation. Crystal phases of the CVD-catalyst were observed by X-ray diffraction (XRD). The morphology and dimensions of the MCNTs were observed by transmission electron microscopy (TEM), concluding that large multiwalled MCNTs were prepared with MNPs inside (spacing of ~0.2 nm) and with a carbon interlayer spacing of ~0.34 nm.

2. Experimental procedure

2.1. Materials and chemicals

Al₂O₃ (particle size = 53-106 μm, BASF) was used as support in the preparation of the CVD-catalyst. Impregnation and co-precipitation processes were considered using Ni(NO₃)₂·6H₂O (99%), Fe(NO₃)₃·9H₂O (98%) and Al(NO₃)₃·9H₂O (99%) salts supplied by VWR Chemicals. NH₄OH (25%) used for precipitation was provided by Panreac. Low-density Polyethylene (LDPE) obtained from Aldrich Chemistry was used as carbon precursor for the growth of carbon nanotubes on the metal CVD-catalysts.

2.2. Preparation of CNTs

Four CVD-catalysts were prepared with Al₂O₃, and Ni, Fe and Al nitrate salts, by wetness impregnation and precipitation processes to assess the effect of these methods on both CVD-catalyst and the resultant CNTs.

The first catalyst (Ni/Al₂O₃-WI) was prepared by wetness impregnation of Al₂O₃ with 1.35 M Ni(NO₃)₂ to obtain 20% NiO over Al₂O₃. The impregnation took place in a lab rotary evaporator R-114 (Buchi) at 70 °C and 72 mbar during *ca.* 3 h. A Ni+Fe/Al₂O₃-WI CVD-catalyst was similarly prepared, but using a solution of 0.42 M Ni(NO₃)₂ and 0.87 M Fe(NO₃)₃. The third catalyst (Ni+Fe/Al₂O₃-CP) was obtained by precipitation of nickel and iron contained in a solution with 0.027 M Ni(NO₃)₂, 0.054 M Fe(NO₃)₃ and 6.28 g of Al₂O₃. For the precipitation, 1 M NH₄(OH) was added dropwise using a peristaltic pump, under constant vigorous stirring until reaching pH 8. Afterwards, possible residues of the precursors were washed-out with distilled water by centrifugation. Ni+Fe+Al-CP CVD-catalyst was prepared by the same method of co-precipitation (dropwise addition of 1 M NH₄(OH)), but using 0.027 M Ni(NO₃)₂, 0.054 M Fe(NO₃)₃ and 0.22 M Al(NO₃)₃. After impregnation or precipitation, the catalysts were dried overnight in oven at 60 °C and sequentially calcined (Thermolyne 6000 Furnace) at the CVD-temperature (800 °C) during 3 h.

CNTs were prepared in a Termolab vertical tubular furnace (*i.d.* = 50 mm, L = 500 mm) with three heating zones controlled independently by EPC3000 controllers (Fig. 1). A crucible containing the PSW is held and located in the upper heating zone. The CVD-catalyst was located in other crucible at the lower heating zone. In a

typical experiment, 5 g of polymer (LDPE was used as model PSW) was loaded in the first crucible and 1 g of catalyst in the second. The experiment was performed at 450 °C in the cracking heating zone and at 850 °C in the CVD zone under a N₂ flow (100 cm³·min⁻¹), during 1 h. Afterwards, the CNT-containing samples were purified with 50 vol% H₂SO₄ at 140 °C during 3 h. Then, the recovered solids were thoroughly washed with distilled water until the neutrality of the rinsing waters, and further dried overnight in oven at 60 °C. The resultant CNTs have been denoted according to the CVD-catalyst used in their growth: CNT@Ni/Al₂O₃-WI, CNT@Ni+Fe/Al₂O₃-WI, CNT@Ni+Fe/Al₂O₃-CP, and CNT@Ni+Fe+Al-CP.

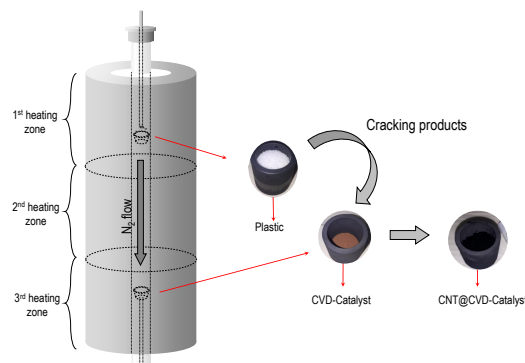


Figure 1. Experimental setup used to prepare the CNTs from plastic by sequential thermal cracking and CVD.

2.3. Characterization techniques

The procedures used for X-ray diffraction (XRD) analysis were described in a previous publication (Santos Silva et al. 2019). The TEM images were obtained using a JEOL 2100, LaB₆ filament, transmission electron microscope operating at 200 kV.

3. Results and discussion

The characteristics of the CNTs produced by CVD depend on the operating conditions (e.g. temperature, time and pressure) and on the nature and load of both carbon source and metallic catalyst (Szabó et al. 2010). In this work, different CVD-catalysts based on Ni, Fe and Al were prepared by wetness impregnation and assessed in the growth of CNTs. The preparation of the CNTs reached yields ranging from 15 to 20% in respect to the quantity of LDPE fed to the system.

Figure 2 shows the XRD diffractograms of the CVD-catalyst, namely Ni/Al₂O₃-WI, Ni+Fe/Al₂O₃-WI, Ni+Fe/Al₂O₃-CP and Ni+Fe+Al-CP, prior to be used in the synthesis of CNTs. As observed, all XRD spectra show diffraction peaks at 2θ = 37.3°, 45.6° and 66.1-66.5°, which correspond to γ-Al₂O₃ (JCPDS Card No. 10-0425) (Tribalis et al. 2016; Wang et al. 2012).

Nickel (II) oxide (JCPDS Card No. 78-0643) shows diffraction peaks at similar 2θ values (Fazlali et al. 2015). However, the presence of Ni₂O₃ (JCPDS Card No. 14-0481) is observed in Ni/Al₂O₃-WI, as revealed by the diffraction peak at 2θ = 31.8° (Sharma et al. 2015). Nickel ferrite, NiFe₂O₄ (JCPDS Card No. 10-0325) is present in

both Ni+Fe/Al₂O₃-WI and Ni+Fe/Al₂O₃-CP materials prepared by impregnation and co-precipitation methods ($2\theta = 30.5^\circ, 44.0^\circ, 54.0^\circ, 58.0^\circ$ and $66.1-66.5^\circ$) (Maleki et al. 2018), being more evident in Ni+Fe/Al₂O₃-CP. In this, the presence of iron and nickel aluminate spinel (JCPDS Card No. 007-0068 and 73-1961, respectively) were mainly identified (Jastrzębska et al. 2015). All materials with iron in their composition show paramagnetic properties due to the presence of NiFe₂O₄.

TEM images showed that different structures of carbon nanotubes (hollow inside) were produced (*cf.* Figure 3). Ni/Al₂O₃-WI lead to produce carbon nanotubes with inner diameters (*i.d.*) ranging from 4 to 10 nm. Ni+Fe/Al₂O₃-WI show wide inner diameters (8–14 nm) distribution and some carbon nanotubes show cup-stacked structures. CVD-catalyst prepared by co-precipitation methods (Ni+Fe/Al₂O₃-CP and Ni+Fe+Al-CP) also show different structures, as helicoidal nanotubes and carbon chains. Ni+Fe/Al₂O₃-CP lead to CNTs with wider diameters distributions (4–12), whereas Ni+Fe+Al-CP allow to produce narrow nanotubes (*i.d.* = 2–12 nm).

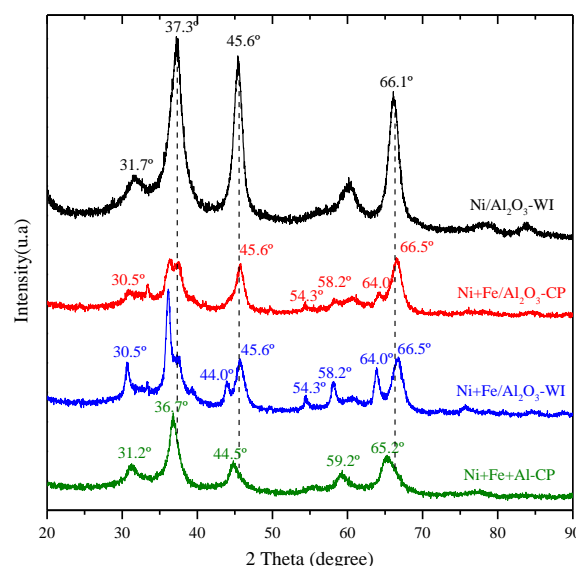
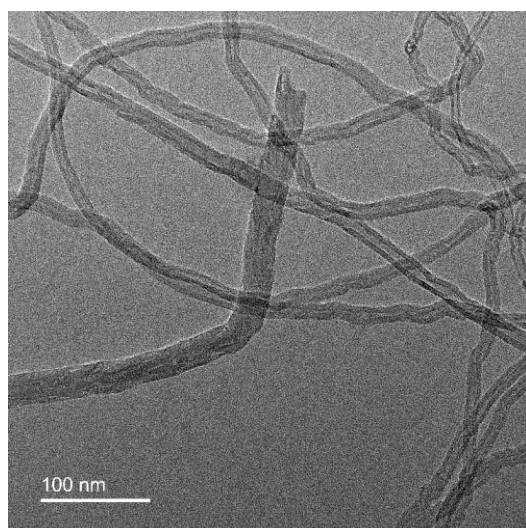
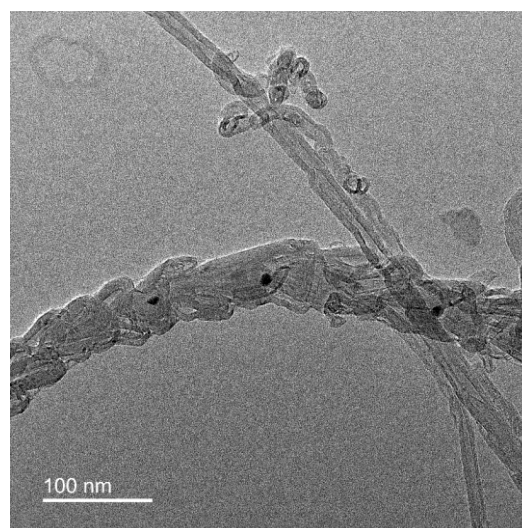


Figure 2. XRD spectra of each CVD-catalyst prepared for the growth of CNTs.

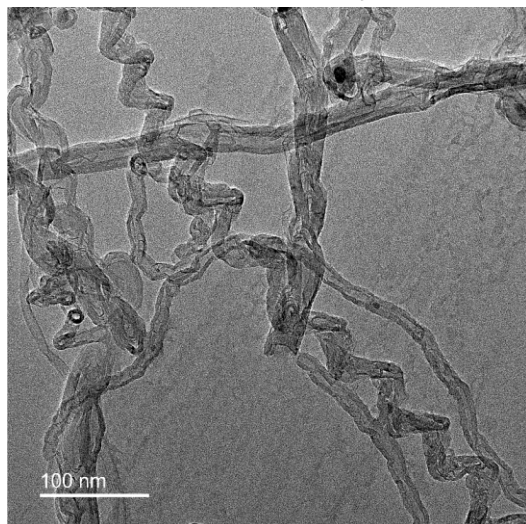
(a) CNT@Ni/Al₂O₃-WI



(b) CNT@Ni+Fe/Al₂O₃-WI



(c) CNT@Ni+Fe/Al₂O₃-CP



(d) CNT@Ni+Fe+Al-CP

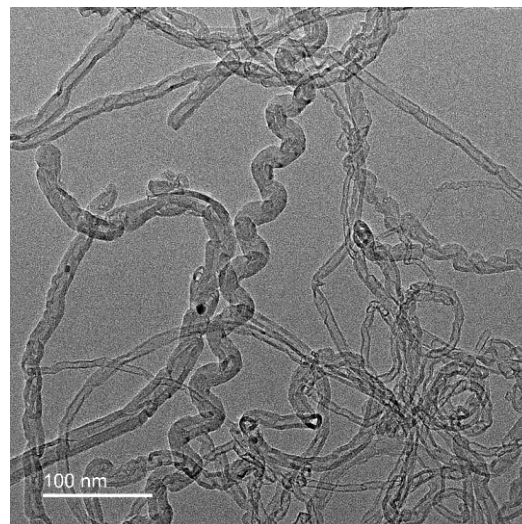


Figure 3. TEM images of the synthesized CNTs prepared from LDPE.

For all materials, Ni-Fe nanoparticles were either found as external aggregates or inside the nanotubes. Encapsulated Ni-Fe nanoparticles with sizes ranging 2–16 nm are typically formed during CVD processes by the reduction of the active phase by carbon sources at high temperatures (Menezes et al. 2015), since encapsulation takes place during the growth of the carbon nanostructures, trapping these catalysts inside the CNTs.

4. Conclusions

A pure polyolefin (LDPE), used as model polymer composing plastic solid wastes, has been successfully transformed through thermal cracking and chemical vapour deposition into magnetic carbon nanotubes (MCNTs). Despite the fact that the materials were washed with acid, paramagnetic properties are observed for the materials due to the embedded magnetic nanoparticles of NiFe₂O₄ in the inner of the carbon nanotubes.

In conclusion, the synthesis of MCNTs from polyolefins is evidenced and can lead to technological alternatives in the treatment of PSWs.

Acknowledgments

This work was financially supported by project "PLASTIC_TO_FUEL&MAT – Upcycling Waste Plastics into Fuel and Carbon Nanomaterials" (PTDC/EQU-EQU/31439/2017), Base Funding - UIDB/50020/2020 of the Associate Laboratory LSRE-LCM - funded by national funds through FCT/MCTES (PIDDAC), and CIMO (UIDB/00690/2020) through FEDER under Program PT2020. Fernanda F. Roman acknowledges the national funding by FCT through the individual research grant SFRH/BD/143224/2019.

References

Aboul-Enein A.A., Awadallah A.E., Abdel-Rahman A.A.H., Haggag A.M. (2018), Synthesis of multi-walled carbon nanotubes via pyrolysis of plastic waste using a two-stage process, *Fullerenes, Nanotubes and Carbon Nanostructures*, **26**,443-450.

Bazargan A., McKay G. (2012), A review – Synthesis of carbon nanotubes from plastic wastes, *Chemical Engineering Journal*, **195-196**,377-391.

Cai N. et al. (2021), Pyrolysis-catalysis of different waste plastics over Fe/Al₂O₃ catalyst: High-value hydrogen, liquid fuels, carbon nanotubes and possible reaction mechanisms, *Energy Conversion and Management*, **229**,113794.

Diaz de Tuesta J.L., F. Machado B., Serp P., T. Silva A.M., Faria J.L., T. Gomes H. (2019), Janus amphiphilic carbon nanotubes as Pickering interfacial catalysts for the treatment of oily wastewater by selective oxidation with hydrogen peroxide, *Catalysis Today*, **356**,205-215.

Fazlali F., Mahjoub A.r., Abazari R. (2015), A new route for synthesis of spherical NiO nanoparticles via emulsion nano-reactors with enhanced photocatalytic activity, *Solid State Sciences*, **48**,263-269.

J. Aguado, Serrano D.P., Escola J.M. (2008), Fuels from Waste Plastics by Thermal and Catalytic Processes: A

Review, *Industrial & Engineering Chemistry Research*, **47**,7982-7992.

Jastrzębska I., Szczerba J., Stożch P., Błachowski A., Ruebenbauer K., Prorok R., Śniezek E. (2015), Crystal structure and Mössbauer study of FeAl₂O₄, *Nukleonika*, **60**,47-49.

Jia J., Veksha A., Lim T.-T., Lisak G. (2020), In situ grown metallic nickel from X–Ni (X=La, Mg, Sr) oxides for converting plastics into carbon nanotubes: Influence of metal–support interaction, *Journal of Cleaner Production*, **258**,120633.

Liu X. et al. (2018), Producing carbon nanotubes from thermochemical conversion of waste plastics using Ni/ceramic based catalyst, *Chemical Engineering Science*, **192**,882-891.

Maleki A., Taherizadeh A.R., Issa H.K., Niroumand B., Allafchian A.R., Ghaei A. (2018), Development of a new magnetic aluminum matrix nanocomposite, *Ceramics International*, **44**,15079-15085.

Menezes H.C. et al. (2015), Magnetic N-doped carbon nanotubes: A versatile and efficient material for the determination of polycyclic aromatic hydrocarbons in environmental water samples, *Analytica chimica acta*, **873**,51-56.

Panahi A., Wei Z., Song G., Levendis Y.A. (2019), Influence of Stainless-Steel Catalyst Substrate Type and Pretreatment on Growing Carbon Nanotubes from Waste Postconsumer Plastics, *Industrial & Engineering Chemistry Research*, **58**,3009-3023.

Passamonti F.J., Sedran U. (2012), Recycling of waste plastics into fuels. LDPE conversion in FCC, *Applied Catalysis B: Environmental*, **125**,499-506.

PlasticsEurope (2021) Plastics – the Facts 2020, An analysis of European plastics production, demand and waste data.

Santos Silva A., Seitovna Kalmakhanova M., Kabykenovna Massalimova B., G. Sgorlon J., Diaz de Tuesta J.L., T. Gomes H. (2019), Wet Peroxide Oxidation of Paracetamol Using Acid Activated and Fe/Co-Pillared Clay Catalysts Prepared from Natural Clays, *Catalysts*, **9**,705.

Sharma A.K., Desnavi S., Dixit C., Varshney U., Sharma A. (2015), Extraction of Nickel Nanoparticles from Electroplating Waste and Their Application in Production of Bio-diesel from Biowaste, *International Journal of Chemical Engineering and Applications*, **6**,156-159.

Szabó A., Perri C., Csató A., Giordano G., Vuono D., Nagy J.B. (2010), Synthesis Methods of Carbon Nanotubes and Related Materials, *Materials*, **3**,3092-3140.

Thompson R.C., Moore C.J., vom Saal F.S., Swan S.H. (2009), Plastics, the environment and human health: current consensus and future trends, *Philosophical transactions of the Royal Society of London Series B, Biological sciences*, **364**,2153-2166.

Tribalis A. et al. (2016), Ni Catalysts Supported on Modified Alumina for Diesel Steam Reforming, *Catalysts*, **6**,11.

Wang Y., Shih K., Jiang X. (2012), Phase transformation during the sintering of γ -alumina and the simulated Ni-laden waste sludge, *Ceramics International*, **38**,1879-1886.

Wen Y., Liu J., Song J., Gong J., Chen H., Tang T. (2015), Conversion of polystyrene into porous carbon sheets and hollow carbon shells over different magnesium oxide templates for efficient removal of methylene blue, *RSC Advances*, **5**,105047-105056.

Zhuo C., Levendis Y.A. (2014), Upcycling Waste Plastics into Carbon Nanomaterials: A Review, *Journal of applied Polymer science*, **131**,39931 (39931-39914).