

Vol. 3 No. 1 (2023): ENP Engineering Science Journal Special Issue "Nanotechnology Engineering"

DOI: <https://doi.org/10.53907/enpesj.v3i1>

Editorial for Special Issue ‘Nanotechnology Engineering’

Azzedine Bousseksou, Jean-Pierre Sauvage

1-2

Magnetic properties and Structural characterization of nanocrystalline Fe-20%A (Ni, Co and Si) alloys powders synthesized by mechanical alloying process

Abderrahmane YOUNES, Abderahim ABADA, Amirouche BOUAMER, Rachid AMRAOUI

3-6

Hybrid materials based on Fe₂O₃/metal-oxide reinforced polyaniline: Synthesis, characterization and their electrochemical properties

Fatima zohra Zeggai, Ilyes Otmane , Hafida Zerigui, Redouane Chebout, Khaldoun Bachari

7-14

Behavior of Materials in the Presence of Particles Additive Technique: A Review

Fares Mohammed Laid REKBI

15-26

Electrochemical Measurements of Ni / Graphene based Nanohybrids for Electrochemical Energy Storage “Supercapacitors”

Ikram Djebablia, Ouanassa GUELLATI, Naima Habib, Aicha Harat, Fahima Djefafli, Assia Nait-Merzoug, Izabella Janowska, Mohamed Guerioune

27-34

Physico-Chemical Properties of Three Synthesized Carbonaceous Nanomaterials (CNTs, GO, Biochar) for Perspective Application: Water / Soil Treatment and Energy Storage

Hanene Araissia, Ouanassa GUELLATI, Fatima Abbaci, Aicha Harat, Jamal El-Haskouri, Dominique Begin, Mohamed Guerioune, Assia Nait-Merzoug

35-41

Goethite Nanofibers /CNTs based Nanocomposites Synthesized by Free-Template Hydrothermal Method and their Physico-Chemical Properties for Energy Storage Application

Sara Djelamda, Fahima Djefafli, Aicha Harat, Assia Nait-Merzoug, Dami Momodu, Ncholu Manyala, Mohamed Guerioune, Ouanassa GUELLATI

42-47

Optoelectronic and Thermoelectric Properties of the Tetragonal Structure of the Halide Perovskite Material RbSeBr₃ used for low-cost Photovoltaic

Rabah Mehyaoui, Karima Benyahia

48-53

Catalytic pyrolysis of high-density polyethylene for the production of carbon nanomaterials: effect of pyrolysis temperature

Salma Belbessai, El-Hadi Benyoussef, Nicolas Abatzoglou

54-58

Editorial for Special Issue “Nanotechnology Engineering”

Azzedine Bousseksou and Jean-Pierre Sauvage

Abstract—This Editorial paper presents the special issue of the ENP Engineering Science Journal special issue on “Nanotechnology Engineering”.

Keywords— Nanotechnology, Engineering.

This special issue presents extended versions of papers selected from the First Symposium of the Algerian Academy of Sciences and Technologies (AAST) on Nanotechnologies that had place on June 26 and 27, 2022 at the M'hamed Bougara University, Boumerdes. Eight papers are accepted after following the ENPESJ review process.

In the article “Magnetic properties and Structural characterization of nanocrystalline Fe-20%A (Ni, Co and Si) alloys powders synthesized by mechanical alloying process” [1] Abderrahmane Younes et al. deal with the preparation and characterization of nanocrystalline Fe-A (Ni, Co, and Si) alloy powders using mechanical alloying technique with Retsch PM 400 high energy planetary ball mill. The evolution of the phases and magnetic properties of the powders are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and vibrating sample magnetometer (VSM) as a function of grinding time. The XRD results indicate that after 20 hours of milling, the FeNi, FeCo, and FeSi phases are completely formed. The lattice deformation of FeSi alloy is 0.7%, and the grain size decreased to 17 nm, 13.5 nm, and 10 nm for FeNi, FeCo, and FeSi, respectively. The VSM results show that the magnetic properties of FeNi, FeCo, and FeSi alloy nanoparticles are influenced by the composition, size, and morphology of the particles.

In the article “Hybrid materials based on Fe₂O₃/metal-oxide reinforced polyaniline: Synthesis, characterization and their electrochemical properties” [2] Fatima Zohra Zeggai et al. develop Polyaniline (PANI)-Fe₂O₃/CuO and PANI - Fe₂O₃/ZnO hybrid materials in situ polymerization at 0°C using ammonium persulfate as oxidant. The resulting products are investigated for their structural properties by X-ray diffraction (XRD), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM), and the results confirm the formation of the hybrid architecture. In addition, the electrochemical properties of the hybrid products are investigated by cyclic voltammetry (CV) and optical properties are determined using UV-Vis Diffuse Reflectance Spectrophotometer (UV-Vis DRS). Compared to PANI/ZnO or CuO, Fe₂O₃/CuO or ZnO exhibit significantly improved

properties. Based on the obtained results, the products thus open the way for a variety of electrical and sensors applications.

In the article “Behavior of Materials in the Presence of Particles Additive Technique: A Review” [3] Fares Mohammed Laid Rekbi reviews the salient features of experimental as well as numerical investigation on characteristics composite materials with adding either micro- or nano-particles, which is one of the ways to express it. The behavior of composites materials such as mechanical enhanced with different form, size, type and nature of particle additives. The bibliography review concludes that it would be important to investigate extensively the features of the aforementioned technique in order to get more discoveries and developments of materials experimentally and numerically. Some contributions have identified the research gaps and deduced that the potential application of particles as additive agents in composites have not been more explored.

In the article “Electrochemical Measurements of Ni / Graphene based Nanohybrids for Electrochemical Energy Storage (Supercapacitors)” [4] Ikram Djebablia et al. deal with the application of new smart nanomaterials for supercapacitors and biosensors has become a vital issue for human and industrial societies. The authors have produced electroactive nanohybrids based on in-situ Ni mono-hydroxide few layers Graphene oxide "GO" using a simple and low cost hydrothermal technique under well-studied thermodynamic conditions (120 and 180 °C growth temperature), for performant supercapacitor devices. They have carried out various electrochemical measurements through Cyclic Voltammetry tests and have marked the important electrochemical properties of these Ni/Graphene nanohybrids in two NaOH electrolyte concentrations (0.1 and 1 M) in order to improve the performance of supercapacitors which have become a socio-economic issue with this nanotechnological development.

In the article “Physico-Chemical Properties of Three Synthesized Carbonaceous Nanomaterials (CNTs, GO, Biochar) for Perspective Application: Water / Soil Treatment and Energy Storage” [5] Hanene Araissia et al. report a comparison of three kinds of nanostructured carbon based smart nanomaterials synthesized at different dimension (1D, 2D and 3D) using physico-chemical growth processes. The obtained nanostructured carbon have shown structural forms in the case of MWNTs and graphene type having 1D and 2D configuration, respectively, as well as an amorphous form in the case of biochar having 3D porous configuration which contains less cohesive bonds than graphene and MWNTs. The two structured ones have shown interesting characteristics of their specific surface area in the range 150-2400 m²/g and functional groups; which open up a wide field of application especially environmental protection and biosensing.

Manuscript received July 20, 2023.

A. Bousseksou is with LCC-CNRS (Director), Toulouse, France (e-mail: azzedine.bousseksou@lcc-toulouse.fr)

J-P. Sauvage, 2016 Nobel Prize in Chemistry, is with University of Strasbourg, France. (e-mail: jpsauvage@unistra.fr)

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.221

In the article "Goethite Nanofibers /CNTs based Nanocomposites Synthesized by Free-Template Hydrothermal Method and their Physico-Chemical Properties for Energy Storage Application" [6] Sara Djelamda et al. report the synthesis of Goethite-NFs/CNTs nanocomposites using hydrothermal method at optimized growth condition. The obtained Goethite nanofibers (NFs) have shown structured triangular base nanofibers with diameter in the range [181 - 363 nm]. Using nested and twisted CNTs (MWNTs type) but fairly homogeneous in diameter around 48 nm, the formation of an assembly of two forms (MWNTs and iron oxide Nanofibers) in nanocomposite configuration confirms the significant improvement of their physico-chemical properties, like the increase in their electrical conductivity proven by their obtained gap energy E_g from 3.12 to 2.50 eV. Consequently, the reached results prove that this kind of iron oxide-NFs/MWNTs based nanocomposites can be excellent candidate as electroactive nanomaterials for energy storage application.

In the article "Optoelectronic and Thermoelectric Properties of the Tetragonal Structure of the Halide Perovskite Material RbSeBr_3 used for low-cost Photovoltaic" [7] Rabah Mehyaoui et al. investigate the Perovskite solar cells. The structural, electronic and optical properties of the tetragonal inorganic halideperovskite RbSeBr_3 are performed using the full potential linearized augmented plane waves (FP-LAPW) method with the PerdewBurke-Ernzerh generalized gradient approximation (PBE-GGA) as well as the local density approximation (LDA) and the modified Becke-Johnson (mBJ-LDA) as exchange correlation potentials using Wien2k code. The thermoelectric properties have been calculated using BoltzTrap code, the obtained results show that the studied compound (RbSeBr_3) has a metallic character and can be used as an absorber in UV-interval.

In the article "Catalytic pyrolysis of high-density polyethylene for the production of carbon nanomaterials: effect of pyrolysis temperature" [8] Salma Belbessai et al. have considered a two-stage reaction process for converting high-density polyethylene (HDPE) into carbon nanofilaments (CNFs) and hydrogen-rich gas. The experiments are performed in a continuous mode in a two-stage quartz reactor: thermal pyrolysis of HDPE followed by the catalytic decomposition of the pyrolysis gases over a nickel catalyst prepared from mining residues. The results showed that the production of carbon nanomaterials (CNMs) and H_2 is optimal at 650 °C, with yields of 70.8 and 38.0 wt%, respectively. Scanning electron microscopy (SEM) revealed the presence of carbon filaments with different diameters and lengths at the three different temperatures. The thermogravimetric analysis (TGA) confirmed that the produced carbon is filamentous, with the presence of amorphous carbon at 700 °C.

REFERENCES

- [1] A. Younes, A. Abada, A. Bouamer and R. Amraoui, "Magnetic properties and Structural characterization of nanocrystalline Fe-20%A (Ni, Co and Si) alloys powders synthesized by mechanical alloying process," ENPESJ, Vol.3, No.1, pp. 3-6, July 2023. DOI: 10.53907/enpesj.v3i1.129
- [2] F. Z. Zeggai, I. Otmane, H. Zerigui, R. Chebout and K. Bachari, "Hybrid materials based on Fe_2O_3 /metal-oxide reinforced polyaniline: Synthesis, characterization and their electrochemical properties," ENPESJ, Vol.3, No.1, pp. 7-14, July 2023. DOI: 10.53907/enpesj.v3i1.181
- [3] F. M. L. Rekbi, "Behavior of Materials in the Presence of Particles Additive Technique: A Review" ENPESJ, Vol.3, No.1, pp. 15-26, July 2023. DOI: 10.53907/enpesj.v3i1.122
- [4] I. Djebablia, O. Guellati, N. Habib, A. Harat, F. Djefafli, A. Nait-Merzoug, I. Janowska and M. Guerioune, "Electrochemical Measurements of Ni / Graphene based Nanohybrids for Electrochemical Energy Storage (Supercapacitors)," ENPESJ, Vol.3, No.1, pp. 27-34, July 2023. DOI: 10.53907/enpesj.v3i1.158
- [5] H. Araissia, O. Guellati, F. Abbaci, A. Harat, J. El-Haskouri, D. Begin, M. Guerioune and A. Nait-Merzoug, "Physico-Chemical Properties of Three Synthesized Carbonaceous Nanomaterials (CNTs, GO, Biochar) for Perspective Application: Water / Soil Treatment and Energy Storage," ENPESJ, Vol.3, No.1, pp. 35-41, July 2023. DOI: 10.53907/enpesj.v3i1.160
- [6] S. Djelamda, F. Djefafli, A. Harat, A. Nait-Merzoug, D. Momodu, N. Manyala, M. Guerioune and O. Guellati, "Goethite Nanofibers /CNTs based Nanocomposites Synthesized by Free-Template Hydrothermal Method and their Physico-Chemical Properties for Energy Storage Application," ENPESJ, Vol.3, No.1, pp. 42-47, July 2023. DOI: 10.53907/enpesj.v3i1.159
- [7] R. Mehyaoui and K. Benyahia "Optoelectronic and Thermoelectric Properties of the Tetragonal Structure of the Halide Perovskite Material RbSeBr_3 used for low-cost Photovoltaic", ENPESJ, Vol.3, No.1, pp. 48-53, July 2023. DOI: 10.53907/enpesj.v3i1.172
- [8] S. Belbessai, E-H. Benyoussef and N. Abatzoglou, "Catalytic pyrolysis of high-density polyethylene for the production of carbon nanomaterials: effect of pyrolysis temperature," ENPESJ, Vol.3, No.1, pp. 54-58, July 2023. DOI: 10.53907/enpesj.v3i1.177



Azzedine Bousseksou received a diploma in Material Physics from the Bab Ezzouar University (Algiers). He also received a DEA in Materials Science from the University of Nantes in 1988 and then obtained a PhD in Materials Science from the Pierre and Marie Curie University in Paris in 1992. He began his career at the CNRS Coordination Chemistry Laboratory in Toulouse as a research fellow in 1993. In January 2003, while in charge of Research at the LCC-CNRS Toulouse, he created and directed the scientific team "Switchable Molecular Materials". Between 2011 and 2013, he was Deputy Director of the LCC-CNRS Toulouse and has been Director since 2013. He has supervised about twenty post-doctoral students and more than thirty theses. He has registered 16 patents, 2 of which are being exploited, and one Startup in incubation. He published over 380 articles with h-index (2023) ~71. He is a member of 4 academies: the French Academy of Sciences (2013), founding member of the Algerian Academy of Science and Technology -AAST- (2015), member of the European Academy of Sciences and arts (2012) and member of the European Academy of sciences (2014). He received several Award such as Prestigious Süe Prize of the French Society of Chemistry, 2020 Korean Magnetic Society Award, 2012 Prix la Recherche, Chemistry section, 2011 Langevin Prize of the French Academy of Sciences (FR), 2009 SCF Co-ordination Chemistry Division Award, 2003.



Jean-Pierre Sauvage, 2016 Nobel Prize in Chemistry, earned his PhD degree from Louis-Pasteur University under the supervision of Jean-Marie Lehn, himself a 1987 laureate of the Nobel Prize in Chemistry. During his doctoral work, he contributed to the first syntheses of the cryptand ligands. After postdoctoral

research with Malcolm L. H. Green, he returned to Strasbourg, where he is now emeritus professor. Sauvage's scientific work has focused on creating molecules that mimic the functions of machines by changing their conformation in response to an external signal. He was elected a correspondent member of the French Academy of Sciences on 26 March 1990, and became a member on 24 November 1997. He is currently emeritus professor at the University of Strasbourg (Unistra). He shared the 2016 Nobel Prize in Chemistry "for the design and synthesis of molecular machines" with Sir J. Fraser Stoddart and Bernard L. Feringa. He was elected a foreign associate of the US National Academy of Sciences in April 2019. As of 2021, Sauvage has an h-index of 109 according to Google Scholar and of 100 according to Scopus

Magnetic properties and Structural characterization of nanocrystalline Fe-20%A (Ni, Co and Si) alloys powders synthesized by mechanical alloying process

Abderrahmane Younes, Abderahim Abada, Amirouche Bouamer and Rachid Amraoui

Abstract– This study focuses on the preparation and characterization of nanocrystalline Fe-A (Ni, Co, and Si) alloy powders using mechanical alloying technique with Retsch PM 400 high energy planetary ball mill. The evolution of the phases and magnetic properties of the powders are investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX), and vibrating sample magnetometer (VSM) as a function of grinding time. The XRD results indicate that after 20 hours of milling, the FeNi, FeCo, and FeSi phases are completely formed. The lattice deformation of FeSi alloy is 0.7%, and the grain size decreases to 17 nm, 13.5 nm, and 10 nm for FeNi, FeCo, and FeSi, respectively. SEM observations of the powder morphologies at different stages of alloy formation are also conducted. Moreover, elemental maps of Fe, Ni, Co, and Si obtained by EDS experiments confirm the XRD results on the evolution of the alloy formation. Finally, the VSM results showed that the magnetic properties of FeNi, FeCo, and FeSi alloy nanoparticles are influenced by the composition, size, and morphology of the particles. Overall, this study provides valuable insights into the preparation and characterization of nanocrystalline Fe-A (Ni, Co, and Si) alloy powders, which may have potential applications in various fields.

Keywords– Nanostructured FeNi, FeCo and FeSi, Structural properties, Magnetic behavior

NOMENCLATURE

VSM	Vibrating Sample Magnetometer.
XRD	X-ray Diffraction.
SEM	Scanning Electronic Microscopy.
EDS	Energy Dispersive Spectroscopy.
Ms	Saturation Magnetization.
Hc	Coercivity.

I. INTRODUCTION

The science and technology of nanocrystalline materials has a significant advance in the recent years. Mechanical alloying is a technique for the synthesis of such materials, which are of interest for several application fields. The study of these materials is a significant feature that provides an indication of the technological development. Fe-A (Ni, Co and Si) alloys have a range of magnetic properties that make them useful for various applications, including high magnetic permeability, high magnetization saturation, and low coercivity field [1-3]. These materials are applied in different areas, for example, magnetic application, biomedical application, and Turbomachinery components [4-6]. Magnetic evaluation, which refers to the use of various testing techniques to investigate magnetic properties of materials, is an essential

tool in different industrial applications owing to its many advantages [7-11]. Several studies have tackled with these techniques to investigate diverse properties compared to conventional techniques. Among the many magnetic testing processes, the analysis of Vibrating Sample Magnetometers (VSM) is a highly sensitive method that can detect variations in chemical composition, lattice strain, and microstructural properties.

The main scientific purpose of this work is to investigate the preparation and characterization of nanocrystalline Fe-20%A (Ni, Co, and Si) alloy powders using mechanical alloying technique. The study aimed to understand the evolution of the phases and magnetic properties of the powders as a function of grinding time. X-ray diffraction, scanning electron microscopy, energy dispersive X-ray, and vibrating sample magnetometer were used to investigate the structural and magnetic properties of the powders. The study is important because nanocrystalline Fe-20%A (Ni, Co, and Si) alloy powders have potential applications in various fields such as magnetic storage devices, catalysts, and sensors. The findings of this study can provide valuable insights into the preparation and characterization of these powders, which can lead to the development of improved materials with desirable properties for specific applications.

II. EXPERIMENTAL PROCEDURE

The synthesis of nanocrystalline Fe-20%A (Ni, Co and Si) was performed in a PM 400 planetary mill with tungsten carbide (WC) pots. The elemental powders were purchased from Sigma Aldrich (USA). The first one is pure iron with a particle size of 80 μm and purity of 99.5%; the second one is pure Ni, Co and Si with a particle size about of 71 μm , 66 μm and 61 μm and 99.98%, 99% and 98% of purity, respectively. Mechanical grinding was done for 20 h; the ball-to-powder mass ratio was 1:10.

Manuscript received September 25, 2022; revised March 13, 2023.

A. Younes and A. Bouamer and R. Amraoui are with Research Center in Industrial Technologies (CRTI), PO Box 64, 16014, Cheraga, Algeria (e-mail: younesabdol1@gmail.com, amirouchebouamer@gmail.com, amrachid21@gmail.com).

A. Abada is with Laboratory of Aeronautic Science, Aeronautic institute, University of Blida 1, Algeria (e-mail: abada_75@yahoo.fr).

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.129

The elaboration of the samples was performed with a speed of 300 r/min for 15 min of work, followed by a 15 min of pause in order to avoid an excessive rise in temperature in the interior of the pots.

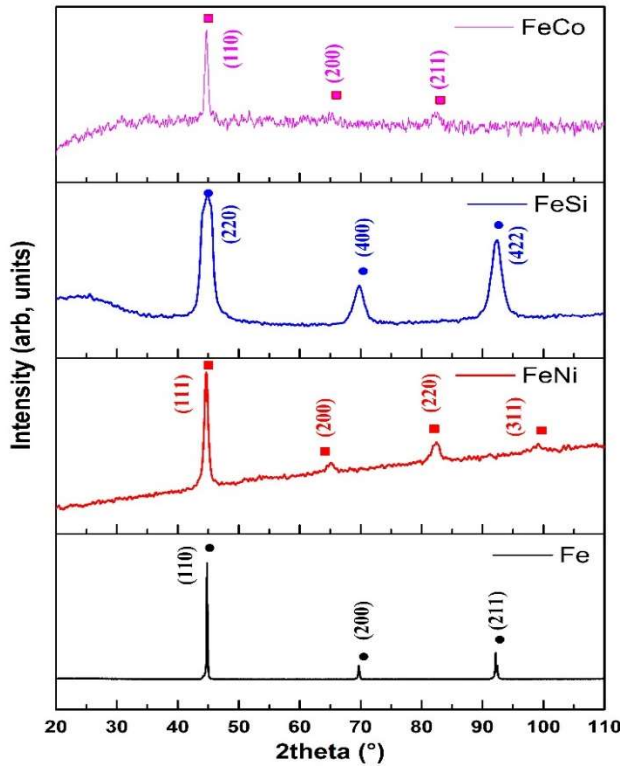


Figure 1. XRD patterns of nanocrystalline milled Fe-20%A alloy for 20 h

The microstructure of the obtained samples was examined using a scanning electron microscope (SEM) - Gemini SEM 300, operated at 30 kV acceleration voltage and equipped with an X-ray dispersive energy spectrometer (EDS) for elemental analysis. The kinetics of the formation during mechanical milling was analyzed using an X-ray diffractometer (XPRT PRO) with Co K α radiation (wavelength $\lambda=1.7889$ Å) in the range of 2θ from 20° to 120° . The magnetic behavior of the samples was analyzed using a vibratory sample magnetometer (model EV9) at room temperature with a sweep rate of 10 Oe/s.

III. RESULTS AND DISCUSSION

III.1. Structural analysis

The kinetics of the formation of nanocrystalline during mechanical grinding was monitored using the X-ray diffraction (XRD) technique. The XRD patterns of the milled powders were evaluated to investigate the variation in structural properties that occurs during mechanical grinding. Figure 1 shows the XRD patterns of nanocrystalline milled Fe-A alloy for 20 h of grinding. For the preliminary powder of Fe, the XRD pattern indicates the existence of a body-centered cubic (bcc) iron. After 20h of milling, appearance of FeNi, FeCo and FeSi solid solution with different intensity and Bragg angle [12-15]. The crystallite size (D) was calculated using the Scherrer equation, which relates the broadening (β) of a diffraction peak to the size of the crystallites. The Scherrer equation is expressed as follows [16-17]:

$$D = K\lambda/\beta\cos\theta \quad (1)$$

where D is the crystallite size, λ is the wavelength of the X-ray radiation used for diffraction (in this case, $\lambda=1.54059$ Å), θ is the diffraction angle (in radians), β is the full width at half

maximum (FWHM) of the diffraction peak, and K is a constant that depends on the shape of the crystallites and is typically taken to be around 0.9. Similarly, the lattice strain (ϵ) was determined using the same diffraction lines and can be calculated from the following equation:

$$\epsilon = (\beta\cos\theta)/\lambda \quad (2)$$

where β is the FWHM of the diffraction peak, θ is the diffraction angle (in radians), and λ is the X-ray wavelength.

Table 1 shows the Crystallite size and Lattice strain of nanocrystalline of Fe-20%A during 20 h of milling. The lattice deformation reached 0.7 % in FeSi alloy, while the grain size decreases to 17 nm, 13.5 nm and 10 nm for FeNi, FeCo and FeSi, respectively.

Table 1. Crystallite size and lattice strain of Fe-20%A

Alloy	Crystallite size D (nm)	Lattice strain ϵ (%)
FeNi	17	0.13
FeCo	13.5	0.36
FeSi	10	0.7

III.2. Morphologies characterization

The morphology of nanocrystalline Fe-A (Ni, Co and Si) during 20h of mechanical grinding is shown in Figure 2. Studies by Davis et al. [18] and Rodriguez et al. [19] have shown that the lamellar structure observed in some particles of nanocrystalline Fe-Ni alloy, as seen in Figure 2(a), is formed by a superposition of Ni and Fe layers. This structure is typical of materials prepared by mechanical milling from ductile (Fe) or brittle (Ni) elements. In a study by Yousefi et al. [8], it was observed that the unmilled FeCo alloy powders consisted of spherical iron particles and skinny, plate-shaped cobalt particles. After mechanical milling, the particles were flattened and changed in shape, likely due to the compression force generated during severe plastic deformation. The resulting particles were smaller than those in the starting mixture, but differences in particle ductility and some larger particles resulting from agglomeration and/or clustering of smaller particles could still be observed.

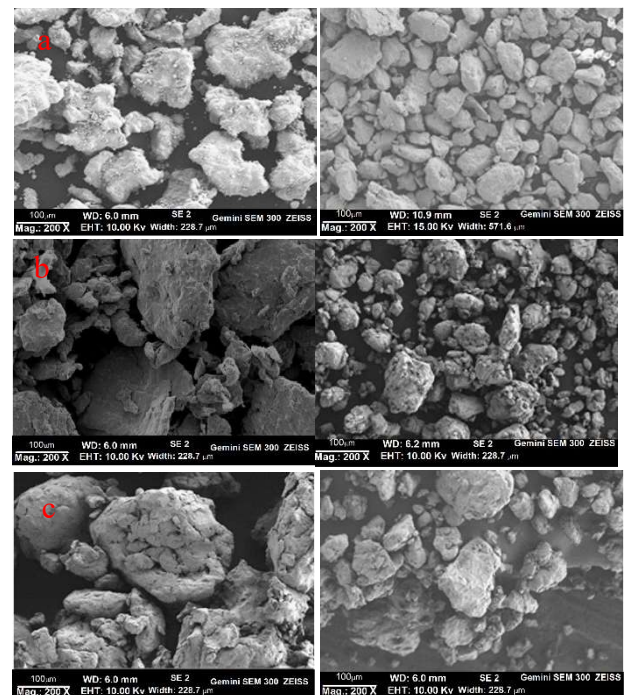


Figure 2. SEM micrographs of nanocrystalline Fe-20%A milled until 20h (a) FeNi, (b) FeCo, and (c) FeSi

The morphology of the FeSi alloy after 20 hours of milling is shown in Figure 2(c). The particles exhibit irregular shapes and varying sizes, which can be attributed to the severe plastic deformation process. The silicon particles were welded and fractured with iron particles to form a nanostructured FeSi alloy. The average particle size of the Fe-Si binary alloy is found to be smaller than that of pure iron and pure silicon. Similar morphologies and grain refinements have been reported in previous studies by Clark et al. [20] and Herting et al. [21].

The energy-dispersive X-ray spectroscopy (EDS) spectrum of the Fe-20%A mixture milled after 20 h is shown in Figure 3. It shows the presence of all elements constituting the alloys. The formation of the Fe-A alloy crystalline structure is given in Figure 3.

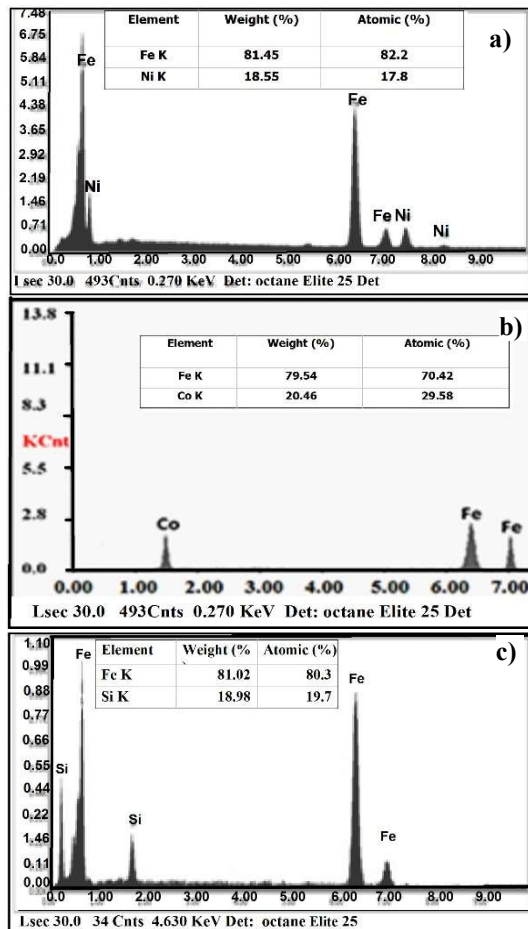


Figure 3. EDS analysis of nanocrystalline Fe-20%A milled until 20h (a) FeNi, (b) FeCo, and (c) FeSi

III.3. Magnetic measurement

Figure 4 shows the hysteresis loops (M-H) for the nanocrystalline Fe-A alloys as a function of the mechanical grinding.

Figure 4 and Table 2 illustrate the magnetic properties of mixtures of FeCo, FeNi, and FeSi alloys. These mixtures exhibit a similar magnetic behavior, with a lower coercivity and higher saturation magnetization. Notably, FeCo shows a significant increase in saturation magnetization, indicating the formation of a solid solution of Fe and Co compared to FeNi and FeSi. Additionally, the maximum coercivity is reached in the FeCo alloy, which is attributed to a decrease in crystallite size and the influence of Co in close proximity to Fe.

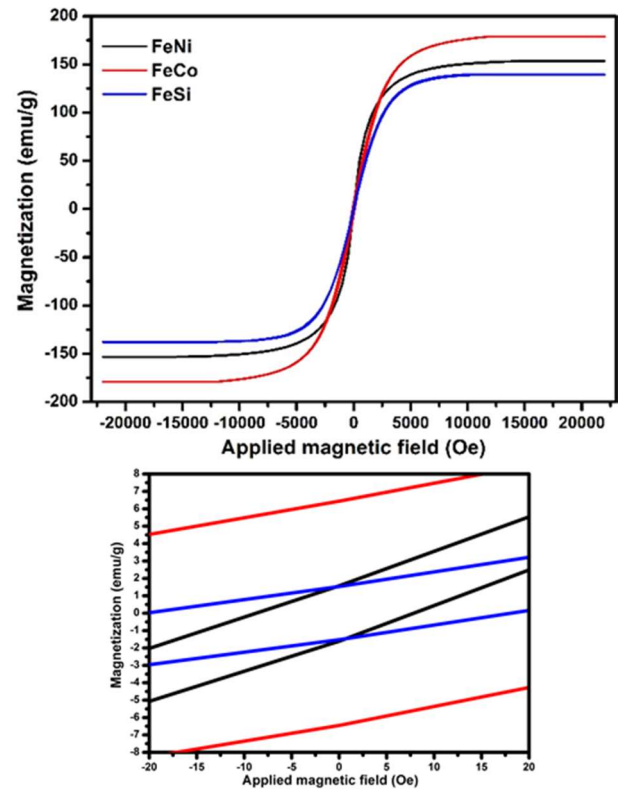


Figure 4. Hysteresis loops of nanocrystalline Fe-20%A (A: Ni, Co and Si) milled until 20h

Table 1. Magnetic parameters of Fe-20%A nanostructured alloys

	FeCo	FeSi	FeNi
Hc (Oe)	96.08	29.38	16.01
Ms (emu/g)	178.24	139.19	153.40
Mr (emu/g)	6.42	1.53	1.59

IV. CONCLUSION

The effective production of a nanocrystalline Fe-20%A (Co, Ni, and Si) alloy through mechanical grinding was confirmed. The magnetic properties of the nanocrystalline Fe-20%A alloy were found to be influenced by various structural and chemical factors, including the crystallite size and the formation of FeCo, FeNi, and FeSi solid solutions. Additionally, the saturation magnetization was found to be highly dependent on the variation in the chemical composition and the introduction of defects during the mechanical alloying process. These findings underscore the importance of carefully controlling the structural and chemical factors during the production of nanocrystalline Fe-20%A alloys to achieve optimal magnetic properties. Future research efforts can focus on optimizing these factors to further enhance the magnetic properties of these alloys for a range of applications.

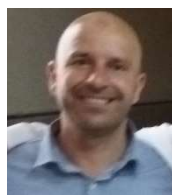
REFERENCES

- [1] A. Younes, N. Kherrouba, Eddy current and magnetic evaluation of nanostructured iron-cobalt produced by ball milling, *Emerging Materials Research*, Vol. 11 no 2, pp. 268-275, June (2022), DOI: 10.1680/jemmr.21.00174

- [2] A. Talaat, J. Egbu, C. Phatak, K. Byerly, M.E. McHenry, P.R. Ohodnicki, Nanostructure refinement and phase formation of flash annealed FeNi-based soft magnetic alloys, *Materials Research Bulletin*, Vol. 152, pp.111839, (2022), DOI:10.1016/j.materresbull.2022.111839
- [3] L.D. Geng, S. Dhoka, I. Goldfarb, R. Pati, Y.M. Jin, Origin of Magnetism in γ -FeSi₂/Si(111) Nanostructures, *Nanomaterials*, Vol. 11 no 4, pp. 849, (2021). DOI:10.3390/nano11040849
- [4] Moustafa, S. F., & Daoush, W. M. (2007). Synthesis of nano-sized Fe-Ni powder by chemical process for magnetic applications. *Journal of materials processing technology*, 181(1-3), 59-63. Doi: 10.1016/j.jmatprotec.2006.03.008
- [5] Behrens, S., Bönnemann, H., Matoussevitch, N., Gorschinski, A., Dinjus, E., Habicht, W., ... & Kempter, V. (2006). Surface engineering of Co and FeCo nanoparticles for biomedical application. *Journal of Physics: Condensed Matter*, 18(38), S2543. DOI 10.1088/0953-8984/18/38/S02
- [6] Krings, A.; Boglietti, A.; Cavignino, A.; Sprague, S. Soft Magnetic Material Status and Trends in Electric Machines. *IEEE Trans. Ind. Electron.* 2017, 64, 2405–2414. DOI:10.1109/TIE.2016.2613844
- [7] M.H. Nateq, S. Kahrobace, M. Kashefi, Use of eddy Current method for determining the thickness of induction-hardened layer in cast iron, *Metal Science and Heat Treatment*, Vol. 55 no 7–8, pp. 370–374, (2013), DOI: 10.1007/s11041-013-9638-0.
- [8] M. Yousefi, S. Sharafi A. Mehrolosseiny, Correlation between structural parameters and magnetic properties of ball milled nano-crystalline Fe-Co-Si powders, *Advanced Powder Technology*, Vol. 25 no 2, pp. 752–760, (2014), DOI: 10.1016/j.appt.2013.11.008.
- [9] G. Cao, D.J. Singh, X.G. Zhang, G. Samolyuk, L. Qiao, C. Parish, K. Jin, Y. Zhang, H. Guo, S. Tang, J. Yi, C. Cantoni, W. Siemons, E.A. Payzant, M. Biegalski, T.Z. Ward, D. Mandrus, G.M. Stocks, Z. Gai, Ferromagnetism and Nonmetallic Transport of Thin-Film α -FeSi₂: A Stabilized Metastable Material, *Phys. Rev. Lett.*, Vol. 114 no 14, pp.147202, April (2015), DOI: 10.1103/PhysRevLett.114.147202.
- [10] J.K. Tripathi, G. Markovich, I. Goldfarb, Self-ordered magnetic α -FeSi₂ nano-stripes on Si (111), *Applied Physics Letters*, Vol. 102 no 25, pp. 251604, (2013), DOI: 10.1063/1.4812239
- [11] A. Hossain, M.K.R. Khan, M.S.I. Sarker, A systematic computational study of electronic, mechanical, and optical properties of Fe_{1-x}Co_x alloy, *Journal of Physics Communications*, Vol. 4 no 4, pp. 045003, (2020), DOI:10.1088/2399-6528/ab843b.
- [12] Crane, R. A., & Scott, T. B. (2013). The effect of vacuum annealing of magnetite and zero-valent Iron nanoparticles on the removal of aqueous uranium. *Journal of Nanotechnology*, 2013.
- [13] Yang, Q., Liu, L., Hui, D., & Chipara, M. (2016). Microstructure, electrical conductivity and microwave absorption properties of γ -FeNi decorated carbon nanotube composites. *Composites Part B: Engineering*, 87, 256-262.
- [14] Li, H., Wang, D., Liang, J. L., Yan, H. Y., Cai, Z. Y., & Reddy, R. G. (2020). Electrochemical Mechanism for the Preparation of Fe-Si Alloys by Melts Electrodeposition. *International Journal of Chemical Reactor Engineering*, 18(2).
- [15] Garnero, C., Pierrot, A., Gatel, C., Marcelot, C., Arenal, R., Florea, I., and Lacroix, L. M. (2021). Single-crystalline body centered FeCo nanooctopods: From one-pot chemical growth to a complex 3D magnetic configuration. *Nano Letters*, 21(8), 3664-3670.
- [16] Harold P. Klug, Leroy E. Alexander, (1974) X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, 2nd Edition.
- [17] Scherrer P, (1918) Bestimmung der Grosse und der inneren Struktur von Kolloidteilchen mittels Rntgenstrahlen .Nachrichten von der Gesellschaft der Wissenschaften zu Gttingen, Mathematisch-Physikalische Klasse 2 : 98.
- [18] R.M. Davis, B. McDermott, C.C. Koch, Mechanical alloying of brittle materials. *Metallurgical Transactions A*, Vol. 19 no 12, pp. 2867-2874, (1988), DOI: 10.1007/BF02647712.
- [19] V.P. Rodriguez, C. Rojas-Ayala, J.M. Medina, P.P. Cabrera, J. Quispe-Marcato, C.V. Landauro, J.R. Tapia, E.M. Baggio-Saitovitch, E.C. Passamani, Fe₅₀Ni₅₀ synthesized by high energy ball milling: A systematic study using X-ray diffraction, EXAFS and Mössbauer methods. *Materials Characterization*, Vol. 149, pp. 249-254, (2019), DOI: 10.1016/j.matchar.2019.01.036.
- [20] Clark, T., and Mathaudhu, S. N. (2019). Microstructure and magnetic properties of dilute nanocrystalline Fe-Si prepared by high energy ball milling. *Journal of Magnetism and Magnetic Materials*, 484, 350-355.
- [21] Herting, G., Jiang, T., Sjöstedt, C., & Odnevall Wallinder, I. (2014). Release of Si from silicon, a ferrosilicon (FeSi) alloy and a synthetic silicate mineral in simulated biological media. *Plos one*, 9(9), e107668.



Abderrahmane Younes born on 23/02/1982 in Tipaza-Algeria. Education: DEUA Aeronautics University of Blida 1- Blida, Engineer Materials Sciences University of Blida 1- Blida, Magister Materials Sciences University Blida 1- Blida, Ph.D. Materials sciences, University of Blida 1- Blida. Current job: Researcher in the Research Centre in Industrial Technologies - CRTI P.O. Box 64, Cheraga 16014 Algiers, Algeria www.crti.dz. Current and previous research interests Nanomaterials characterization by NDT techniques.



Abderahim Abada born on 10/02/1975 in Blida-Algeria. Education: Engineer Aeronautics University of Blida 1- Blida, Magister Aeronautics University of Blida 1- Blida, Ph.D. Aeronautics University Blida 1- Blida. Current job: Laboratory of Aeronautic Science, University of Saad Dahleb Blida, Algeria. www.univ-blida.dz. Current and previous research interests Nanomaterials characterization by NDT techniques.



Amirouche Bouamer born on 27/10/1976 in Tizi- Ouzou-Algeria. Education: D.E.S Solid State Physics, Tizi Ouzou university, Magister Physics of Materials Bab Ezzouar university (USTHB), Ph.D. Physics of Materials Bab Ezzouar university (USTHB), Algiers. Current job: Researcher in the Research Centre in Industrial Technologies - CRTI P.O. Box 64, Cheraga 16014 Algiers, Algeria www.crti.dz. Current and previous research interests Nanocomposite characterization by NDT techniques.



Rachid Amraoui born on 22/11/1984 in Medea-Algeria. Education: Engineer Electronics, University Blida 1- Blida, Magister Electrical Engineering, University of Mostaganem, P h.D. Physics, University Blida 1- Blida. Current job: Researcher in the Research Centre in Industrial Technologies- CRTI P.O. Box 64, Cheraga 16014 Algiers, Algeria www.crti.dz. Current and previous research interests Nanomaterials characterization by NDT techniques.

Hybrid materials based on Fe₂O₃/metal-oxide reinforced polyaniline: Synthesis, characterization and their electrochemical properties

Fatima Zohra Zeggai, Ilyes Otmane, Hafida Zerigui, Redouane Chebout and Khaldoun Bachari

Abstract– Polyaniline (PANI)-Fe₂O₃/CuO and PANI -Fe₂O₃/ZnO hybrid materials were developed and prepared by in situ polymerization at 0°C using ammonium persulfate as oxidant. The resulting products are investigated for their structural properties by X-ray diffraction (XRD), Fourier transform infrared (FTIR), and scanning electron microscopy (SEM), and the results confirm the formation of the hybrid architecture. In addition, the electrochemical properties of the hybrid products are investigated by cyclic voltammetry (CV) and optical properties were determined using UV-Vis Diffuse Reflectance Spectrophotometer (UV-Vis DRS). Compared to PANI/ZnO or CuO, Fe₂O₃/CuO or ZnO exhibit significantly improved properties. Based on the obtained results, the products thus open the way for a variety of electrical and sensors applications.

Keywords– Polyaniline, metal oxide, in-situ polymerization, hybrid material, electrochemical properties.

NOMENCLATURE

PANI	Polyaniline.
APS	Ammonium persulfate.
XRD	X-ray diffraction.
FTIR	Fourier transform infrared.
SEM	Scanning electron microscopy.
UV-vis	Ultraviolet-visible spectroscopy
CV	Cyclic Voltammetry.
ECPs	Electronically conducting polymers
CuO	Copper oxide
ZnO	Zinc oxide
JCPDS	Joint Committee of Powder Diffractions Standards

I. INTRODUCTION

Electronically conducting polymers (ECPs) continue to be of great interest and importance as components for promising applications in energy storage, electrocatalysis, organic electrochemistry, bioelectrochemistry, photoelectrochemistry, electroanalysis, sensors, microsystems engineering, electronic devices, microwave shielding and corrosion protection, etc. Polymeric materials and their composites are capable of changing their structure and properties during reaction with

the environment. Among conducting polymers, polyaniline (PANI) exhibits excellent electrical conductivities and thermal stability [1-2]. It has promising applications in various technological fields such as energy storage [3], electronic and optical devices [4], sensors [5-6], corrosion protection [7] and many more [8-9].

Several studies have been conducted on conductive polymers hybridized with metal oxides to produce functional nanomaterials with excellent properties not only for their intriguing structural characterization but also for their potential functional applications in advanced technologies, such as adsorption, separation, gas storage, antistatic coatings, electrochemical displays, sensors, catalysis, redox capacitors, electromagnetic shielding, etc. Understanding the interactions between the polymer matrix and the metallic filler is essential for the technological implementation of synthesis and engineering of hybrid structures with different dimensions, collective properties at the micro/nanoscale, and predictable physical and mechanical responses to the polymer-metal filler interface. The concept of hybridizing the properties of nanocomposites to form an extraordinary nanomaterial (with the advantages that are not just the sum of the individual contributions) is a famous, renowned technology. Current studies mostly focus on binary metal oxides because they have complementary properties, such as TiO₂, Fe₂O₃, ZnO, ZrO₂, V₂O₅, NiO and Al₂O₃ have been widely studied as nanomaterials for semiconductors [10-14]

The aim of this work was to prepare various hybrid materials PANI /CuO, PANI /ZnO, PANI-Fe₂O₃/CuO, PANI -Fe₂O₃/ZnO by in situ polymerization method using ammonium persulfate as oxidant and to investigate the effects of metal oxides on the surface morphology and properties of PANI. It is also important to find an optimal value for the addition of metal oxide to obtain a perfect hybrid nanomaterial. The organic-inorganic materials were confirmed by various analyses such as: XRD, FT-IR, SEM and UV-vis. The electrochemical behaviour was investigated by cyclic voltammetry. Moreover, the results could be promising for the fabrication of new functional materials, such as organic devices based on metal oxide integrating conducting polymers.

Manuscript received February 8, 2023; revised April 9, 2023.

F.Z. Zeggai, R. Chebout and K. Bachari are with the materials chemistry division, Scientific and Technical Research Center in physico-chemical analyses CRAPC, Bou-ismail Tipaza, ALGERIA (e-mail: zeggai.fatimazohra@crapc.dz, rchebout@crapc.dz, khaldoun.bachari@crapc.dz).

I.Otmane is with the Research laboratory on physico-chemistry of surfaces and interfaces (LRPCSI), University of August 20, 1955-Skikda, ALGERIA and the polymer chemistry laboratory (LCP), University of Ahmed Ben-Bella Oran1, ALGERIA (e-mail: i.otmane@univ-skikda.dz).

H. Zerigui is with the polymer chemistry laboratory (LCP), University of Ahmed Ben-Bella Oran1, ALGERIA, (e-mail: dida-hafida@hotmail.com).

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.181

II. METHODOLOGY

II.1. Apparatus

Fourier Transform Infrared (FT-IR) spectroscopy spectra were recorded using Alpha Bruker. The scanning was performed between 4000 and 400 cm⁻¹ for 32 times with a resolution of 4 cm⁻¹. All spectra were baseline-corrected with Opus software.

The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer DAVINCI model, operating in Bragg–Brentano geometry, with anode using Cu K α as radiation source ($\lambda = 1.5418 \text{ \AA}$).

The ultraviolet–visible diffuse reflectance spectra measurements were recorded using a SPECORD 210 PLUS - 223F1138 UV-Vis spectrophotometer.

Electrochemical properties were carried out using a conventional cell of three electrodes. The counter and reference electrodes were a platinum foil and a hydrogen reversible electrode (RHE), respectively. The entire electrochemical test was carried using the Dimethyl Sulfoxide (DMSO), 50 μL of this solution were cast over graphite carbon electrodes and the solvent evaporated to create polymeric films. The electrolyte used was tetrabutylammonium hexafluorophosphate (TBAPF₆) and all experiments were carried out at 50 mV/s.

Scanning Electron Microscopy (SEM) analysis of nanocomposites powder was performed on a Quanta FEG 250 instrument (FEI, Hillsboro). A tiny amount of material should be collected with a spoon and allowed to fall on a carbon or aluminium holder. Excess particles should then be sprayed away, and the sample should then be coated for imaging.

II.2. Materials

The Aniline monomer employed for the polymerization reaction, ammonium persulfate (APS), copper oxide (CuO, black powder, purity 99%), zinc oxide (ZnO, white powder, purity 99%) were obtained from the company Sigma Aldrich. Di-iron trioxide (Fe₂O₃, reddish powder, purity 95-98%) was purchased from Biochem-Chemopharma. Sulfuric acid was purchased from Merck. All solutions were prepared with distilled water.

II.3. Preparation of the PANI/CuO, PANI/ZnO, PANI-Fe₂O₃/CuO, PANI -Fe₂O₃/ZnO hybrid nanocomposites

Polyaniline/(CuO or ZnO) samples were prepared by in situ oxidative polymerization. In a typical experimental procedure, the polymerization reaction was carried out at 0°C. The amount of CuO or ZnO (1%, 3%, and 5% of the molar weight of the aniline monomer) was added to the aniline monomer (0.022 M) in a 100-ml flask, followed by an oxidizing solution of ammonium persulfate (0.022M) with drop wise aqueous solution of H₂SO₄ (1 M), and the mixture was stirred for 24 hours. PANI-Fe₂O₃/CuO, PANI -Fe₂O₃/ZnO hybrid samples were prepared in the same manner as the previous samples, with Fe₂O₃ (0.5 g) added to all of them.

III. RESULTS AND DISCUSSION

III.1. Vibrational characterization by FT-IR spectroscopy

The representative FT-IR spectra of all samples were given in Figs.1, 2, and 3. The polymerization reaction of aniline is

initiated by an external oxidizing agent (APS) and combined with metal oxide such as CuO or ZnO as Fe₂O₃.

Evidence for the polymerization of aniline is provided by FT-IR spectroscopy. For comparison, a bulk polyaniline was first synthesized by the same method used for composites (in-situ). 0.2 ml (220 mmol) of aniline was added to 0.49 g (220 mmol) of ammonium persulfate in 100 ml of distilled water, then 5 ml of 1M H₂SO₄ was added dropwise to the previous solution. The mixture was stirred at 0°C for 24 hours and finally filtered, washed with distilled water and dried at room temperature. The FT-IR spectrum of polyaniline in Fig.3 exhibits the characteristic peaks found at 3491-3426, 2361, 1544, 1440, and 1284 cm⁻¹ are assigned to N-H stretching, C=N stretching, the ring mode of quinoid structures, the benzoid structure, and C-N stretching of secondary aromatic amine respectively [15-17].

The FT-IR spectra of Pani/CuO and Pani/ZnO at (3, 5, and 7%) are shown in Figs.1 and 2. The FT-IR spectra of the samples show the characteristic vibrations of polyaniline, which agree well with those of chemically synthesized polyaniline. The observed main peaks in the range 411-876 cm⁻¹ characterize the Zn-O-Zn and Zn-O stretching [18]. Samaele et al [19] and Prasad et al [20] reported similar FT-IR spectra of zinc oxide nanoparticles in their studies. For CuO nanoparticles, the absorption bands in the low frequency region of spectra located in the range 553-794 cm⁻¹ confirm the successful deposition of copper oxide [21]. In addition, one other characteristic peak of CuONPs was observed at 1551 cm⁻¹ shows the Cu–O symmetrical stretching.

Figs.1 and 2 shows the FT-IR spectra of the ternary hybrid materials PANI-Fe₂O₃/CuO, PANI-Fe₂O₃/ZnO. The peak of 1518 cm⁻¹ and 1639 cm⁻¹ represent C-C stretching between quinone ring (Q) and benzene ring (N) on PANI, respectively. The absorption band at 1215 cm⁻¹ is C-N stretching of benzene ring, while the peak at 1088 cm⁻¹ is attributed to C-H bending vibration [22]. However, in the PANI-Fe₂O₃/CuO these peaks are small and intense, perhaps due to the effect of Fe₂O₃ on the samples. The presence of copper and zinc oxides was confirmed by their characteristic peak. Two very intense absorption peaks at 517 cm⁻¹ and 434 cm⁻¹ can be distinguished, corresponding to Fe-O bonds in iron oxide. This might be attributed to the strong mutual interactions of hydrogen bonding between the Fe–O of Fe₂O₃ and N-H group of PANI [23].

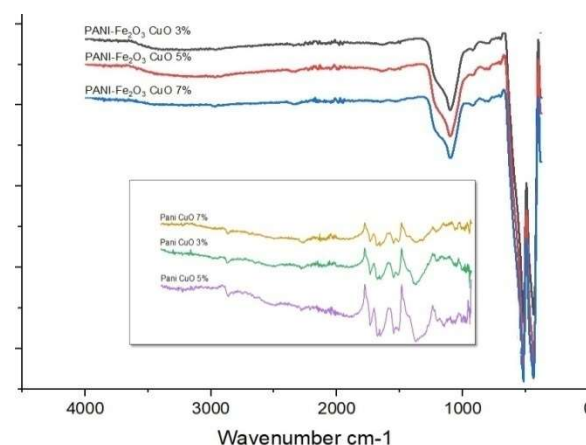


Fig. 1: FT-IR spectra of the Pani-CuO (3%,5%,7%), and hybrid nanocomposites Pani-Fe₂O₃/CuO (3%,5%,7%).

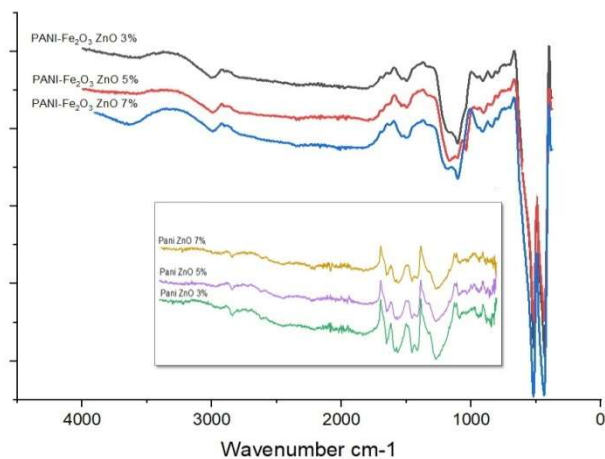


Fig. 2: FT-IR spectra of the Pani- ZnO (3%,5%,7%), and hybrid nanocomposites Pani-Fe₂O₃/ZnO (3%,5%,7%).

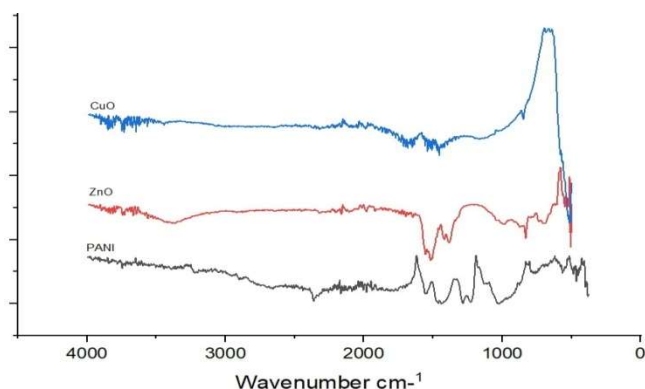


Fig. 3: FT-IR spectra of copper oxide, zinc oxide and Polyaniline.

III.2. XRD spectroscopy

The XRD patterns of ZnO, CuO, and Fe₂O₃ nanoparticle, pure PANI and PANI/CuO, PANI/ZnO, PANI-Fe₂O₃/CuO, PANI-Fe₂O₃/ZnO nanocomposites with the different loading amount of ZnO and CuO (3, 5, and 7%) were shown in Figs.4, 5, and 6.

The bulk PANI XRD diagram is shown in Fig.4. The PANI peak diffracted at an angle of $2\theta = 20.43^\circ$ and $2\theta = 25.27^\circ$ with a d-spacing of 4.35 Å and 3.52 Å, respectively, corresponding to the (200) and (101) planes. The figure shows the low crystallinity of polyaniline due to the repetition of benzenoid and quinoid rings in its chains [24].

The analysis of XRD pattern of ZnO shows the characteristics peaks at $2\theta = 31.84^\circ, 34.52^\circ, 36.38^\circ, 47.64^\circ, 56.70^\circ, 63.06^\circ, 68.10^\circ, \text{ and } 69.18^\circ$ corresponding to crystal planes (100) (002) (101) (102) (110) (103) (112) and (201), respectively, were associated with the hexagonal crystal structure of ZnO. All diffraction peaks are in agreement with those of the wurtzite hexagon structure of ZnO prepared [25]. The values given for ZnO are related to JCPDS #36-1451. It also confirms that the nanoparticle produced was free of impurities because it does not contain characteristic peaks other than those of zinc oxide [26].

The characteristics peaks of CuO comes at $2\theta = 32.49^\circ, 35.56^\circ, 38.68^\circ, 46.23^\circ, \text{ and } 48.76^\circ$ correspond to crystal planes (110), (-111), (200), (-112), and (-202), respectively. The intensities and positions of the observed diffraction peaks agree well with those published in JCPDS #41-0254. This result suggests that we have a single phase of CuO with a monoclinic structure, which is consistent with the literature [27]. The profiles of the main diffraction peaks reflect the high degree of crystallinity of the synthesized CuO particles. No

other phases such as Cu₂O and Cu(OH)₂ were observed, which means that the prepared powder is CuO with very high purity.

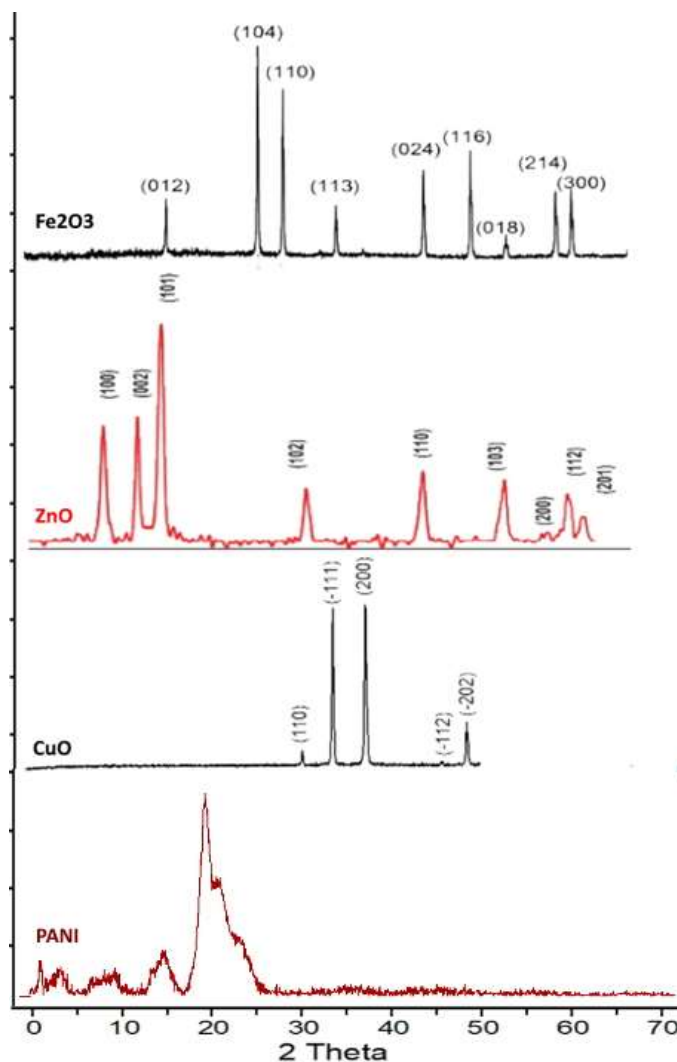


Fig.4: XRD diffraction patterns of PANI, CuO, ZnO and Fe₂O₃.

The hematite phase peaks obtained in the (XRD) pattern of the Fe₂O₃ sample are at $2\theta = 23.15^\circ, 33.21^\circ, 36.11^\circ, 41.17^\circ, 49.31^\circ, 54.12^\circ, 57.20^\circ, 62.35^\circ, \text{ and } 64.10^\circ$; they are associated with levels (012), (104), (110), (113), (024), (116), (214) and (300), respectively. The diffraction peaks are easily assigned to the rhombohedral (hexagonal) structures of the α -Fe₂O₃ phase corresponding to JCPDS number 33-0664 [28].

The XRD patterns of PANI/CuO, PANI/ZnO nanocomposites with the different loading amount of ZnO and CuO (3, 5, and 7%) were shown in Figs. 5 and 6. It can be found that the XRD pattern of the PANI /CuO composite has diffraction peaks around $2\theta \sim 19.29^\circ, 20.782^\circ \text{ and } 26.53^\circ$, which are related to (-111), (-102) and (020), respectively. The diffraction peaks in the preferred directions (-111) and (-102) refer to CuO [27] and the peak (020) refers to PANI. It can also be found that the lattice constants a, b and c and the crystallite size of PANI /CuO composite are larger than those of pure CuO and PANI, confirming the formation of nanocomposites (polymer/CuO) by in situ polymerization [29]. It can be seen that the XRD patterns of PANI /ZnO nanocomposites with 7% ZnO content show good crystallinity. This is due to the presence of ZnO nanoparticles and has a significant effect on the diffraction pattern of PANI due to the formation of hydrogen bonds between H-N and oxygen of ZnO [24]. According to Fig. 6, two distinct sharp peaks at $2\theta = 19.28^\circ \text{ and } 26.83^\circ$ are negligibly shifted with levels (010) and (200), respectively, but their intensity

increases due to the enhancement of ZnO nanoparticles in the matrix PANI. In addition, a peak at $2\theta = 25.44^\circ$ appears with level (102) associated with PANI and its intensity is increased by the addition of ZnO nanoparticles. The XRD results confirm the effect of ZnO nanoparticles in PANI -ZnO nanocomposites, which means that there is an interaction between ZnO nanoparticles and PANI.

However, the XRD pattern of the PANI-Fe₂O₃/ZnO or CuO composite (Figs.5, 6) shows a crystalline phase almost similar to the free Fe₂O₃ with an average particle size, confirming the good enrichment of Fe₂O₃ nanoparticles in the PANI matrix. When comparing the new peaks with JCPDS number 33-0664, they were found to belong to (Fe₂O₃) with a hexagonal phase. With the addition of (Fe₂O₃), an increase in the height and sharpness of the peaks was observed, which led to an increase in the crystallization of the obtained materials. We note a strong preferred orientation of the (104) and (110) planes and a slight shift in the intensity of the peaks, with the PANI-Fe₂O₃/ZnO 7% showing the strongest intensity. All XRD patterns are perfectly aligned with the rhombohedral Fe₂O₃ with unit cell parameters $a=b = 5.036 \text{ \AA}$, $c = 13.75 \text{ \AA}$.

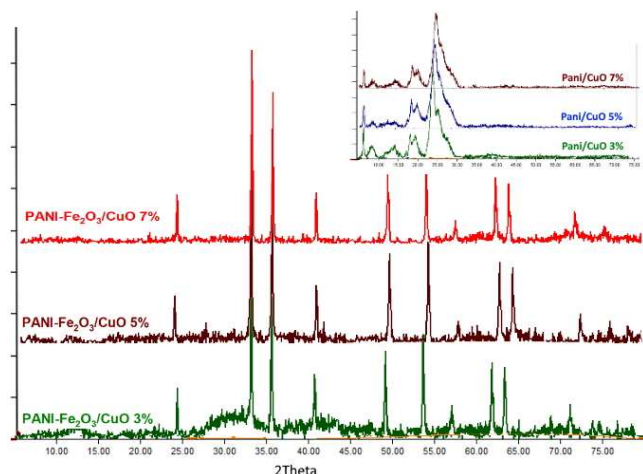


Fig.5: X-ray diffraction patterns of PANI/CuO, PANI-Fe₂O₃/CuO nanocomposites (3, 5, and 7%).

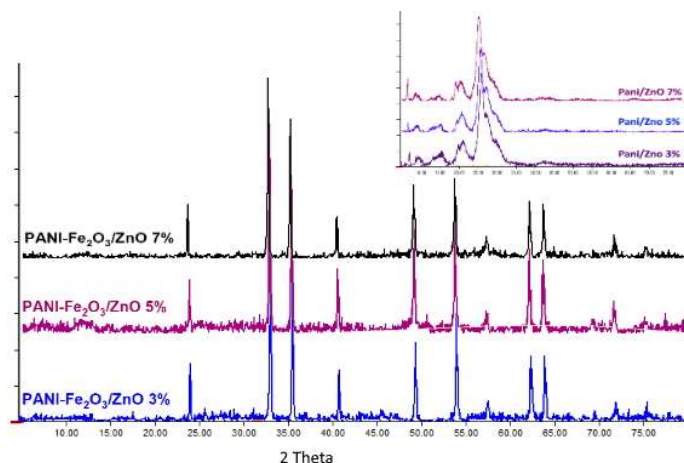


Fig.6: X-ray diffraction patterns of PANI/ZnO, PANI-Fe₂O₃/ZnO nanocomposites (3, 5, and 7%).

We note an increase in intensity as the weight percentage increases, i.e. PANI-Fe₂O₃/CuO 7% represents the strongest intensity. In the XRD patterns of the nanocomposites PANI-Fe₂O₃/ZnO and PANI-Fe₂O₃/CuO, only the peaks associated with the structure of α -Fe₂O₃ can be seen. This confirms the previous results of FTIR, the effect of Fe₂O₃.

III.3. Scanning electron microscopy (SEM)

Figs.7, 8 & 9 showed the surface morphologies of the bulk PANI, PANI/ZnO-7%, PANI/CuO-7%, PANI-Fe₂O₃/CuO-7% and PANI-Fe₂O₃/ZnO-7% nanocomposites. The majority of the grains and flakes in Pani's SEM picture are randomly constructed and have edges. The building also appears to be more porous (Fig.7 (A₁, A₂)). With the use of ImageJ software, the porosity percentage of 31.53% was confirmed. SEM-image (Fig.8 (B & C)) of nano PANI/ZnO-7%, PANI/CuO-7% composites indicate that the incorporation of ZnO & CuO nanoparticles in PANI has a significant effect on the morphology. A decrease in the porosity of PANI can be seen, indicating the dispersion of ZnO & CuO nanoparticles in the PANI matrix. Also, the appearance of certain solid blocks can be seen, which is due to the presence of oxide particles that increase the crystallinity of the composite materials. The micrographs of PANI-Fe₂O₃/CuO-7% and PANI-Fe₂O₃/ZnO-7% (Fig.9 (D & E)) show spherical shapes; PANI-Fe₂O₃/CuO-7% has irregular shapes of grains, while the SEM image of the PANI-Fe₂O₃/ZnO-7% composite shows a completely different picture, where the surface composed of agglomerated, uniform, and spherical grains with a narrow size distribution. This can be attributed to the fact that the Fe₂O₃ nanoparticles act as nuclei during the polymerization of aniline, and cause interaction between the PANI matrix and the oxide particles.

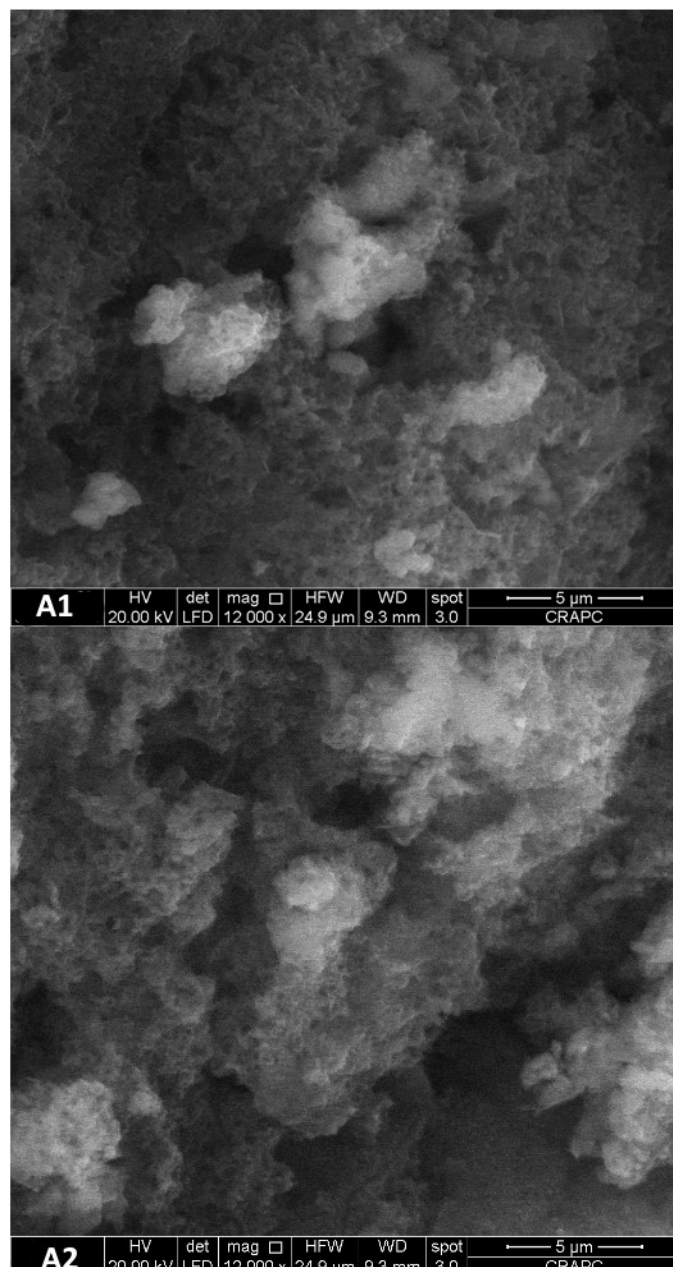


Fig.7: SEM micrograph of: (A₁, A₂) bulk PANI (5 μm).

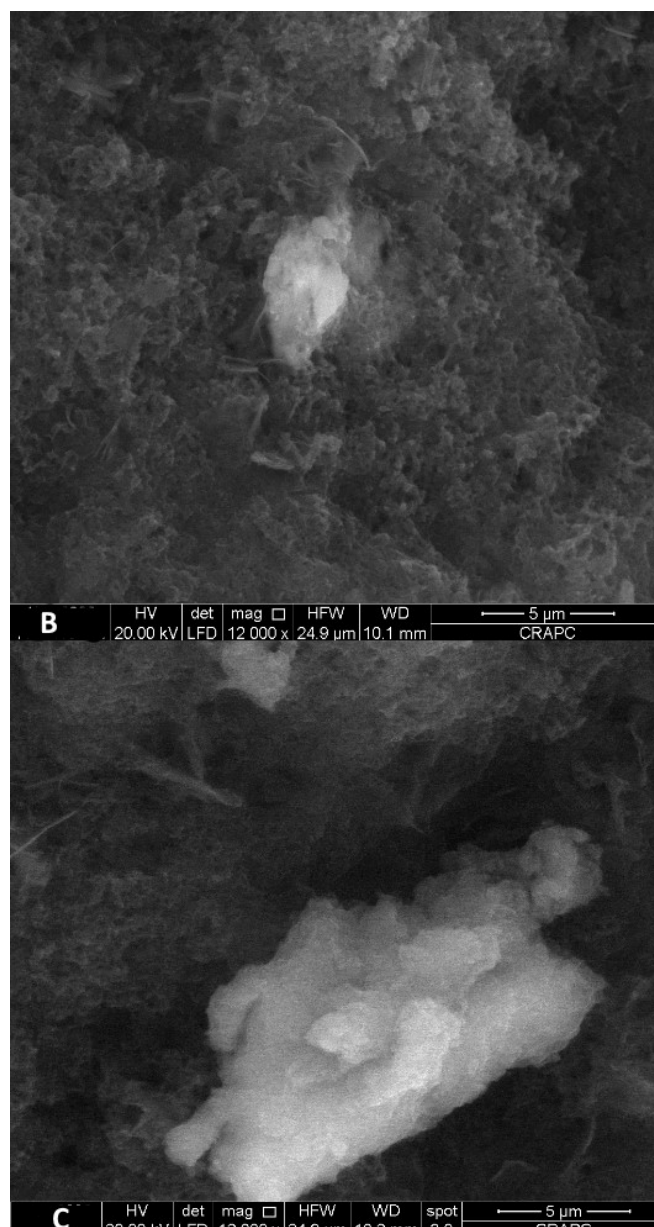


Fig.8: SEM micrograph of: (b) PANI/ZnO 7%, (c) PANI/CuO-7% nanocomposites (at 5μm).

III.4. Cyclic voltammetry tests

The cyclic voltammetry (CV) curves of bulk PANI and PANI/ZnO, PANI/CuO, PANI-Fe₂O₃/CuO and PANI-Fe₂O₃/ZnO samples with the weight of ZnO/CuO (7%) were shown in Figs. 10 & 11.

Several factors may influence the course of electropolymerization by changing its potential. Thus includes the electrolyte concentration, the potential range (especially positive limit), the potential scan rate and the electrode material.

The cyclic voltammograms (Fig.10) show two anodic peaks at positive potentials, observed at $E_{pa1} = -0.638$ V and $E_{pa2} = 0.135$ V, respectively, and two cathodic peaks at negative potentials, observed at $E_{pc1} = -0.743$ V and $E_{pc2} = 0.139$ V, corresponding to different oxidation and reduction states of PANI. The first redox peak corresponds to the transition from leucoemeraldine (LE) to emeraldine (EM), and the second redox peak indicates the transition from EM to pernigraniline (PG). The CV shape of the bulk PANI is similar to that of the literature [30].

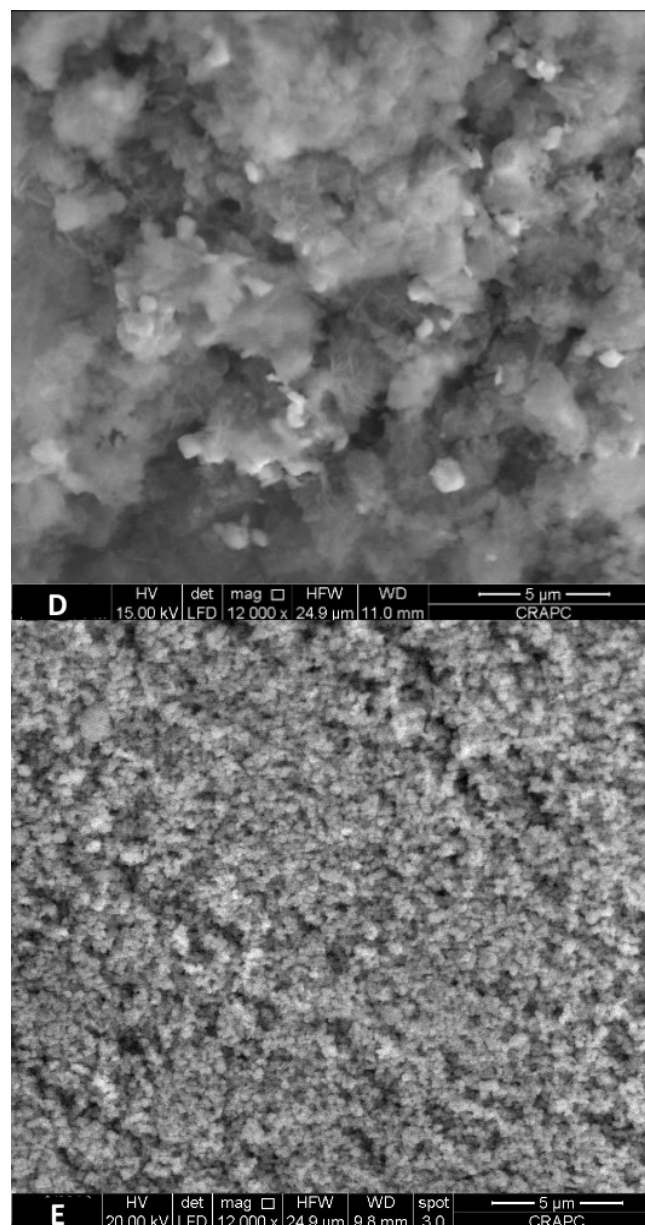


Fig.9: SEM micrograph of: (d) PANI-Fe₂O₃/CuO-7% and (e) PANI-Fe₂O₃/ZnO-7% nanocomposites

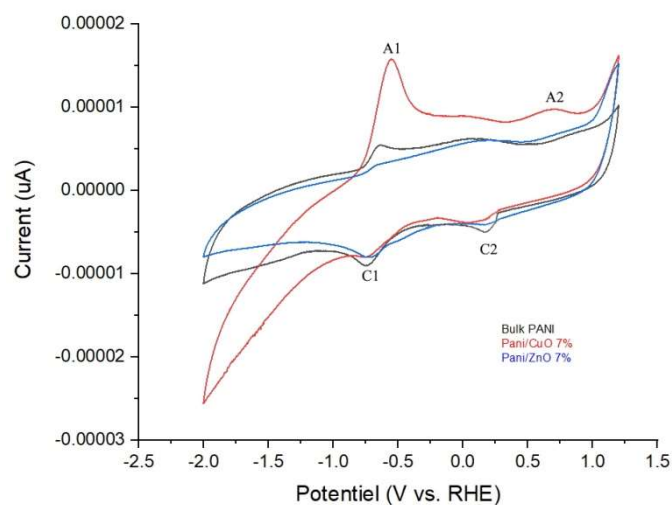


Fig. 10 Cyclic voltammograms recorded in DMSO with TBAPF6 as the supporting electrolyte of: bulk PANI, PANI/CuO (7%) and PANI/ZnO (7%) nanocomposites. Scan rate 50 mV s⁻¹.

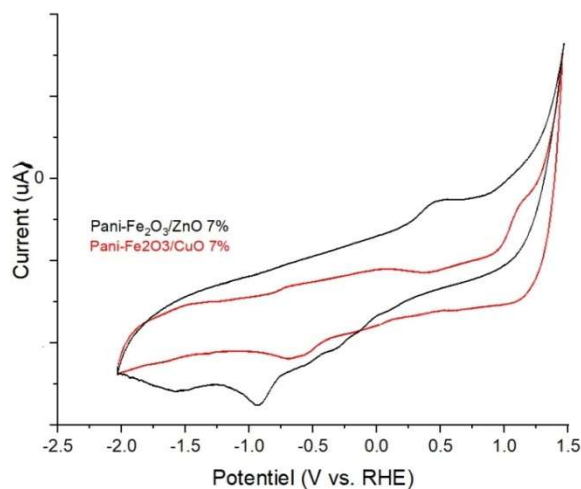


Fig. 11 Cyclic voltammograms recorded in DMSO with TBAPF6 as the supporting electrolyte of: PANI-Fe₂O₃/CuO (7%) and PANI-Fe₂O₃/ZnO (7%) nanocomposites. Scan rate 50 mV s⁻¹.

The CVs of PANI /ZnO and PANI /CuO nanocomposites in Fig.10 show the same shape as those of bulk PANI, but with a decrease in the current intensity of the cathodic and anodic peaks. A slight decrease was observed in the presence of ZnO nanoparticles, but it was particularly pronounced for CuO nanoparticles. This phenomenon was accompanied by a slight shift of the cathodic peak potential toward more positive values, which can be attributed to the modification of the surface electrode by incorporating CuO and ZnO nanoparticles into the PANI.

Therefore, the dispersed CuO, ZnO and Fe₂O₃ affect the electrochemical deposition and properties of PANI (Fig.11). In the case of PANI-Fe₂O₃/CuO (7%) shows three oxidation and three reduction peaks. First oxidation peak represents polyleucoemeraldine (-0.668 V) which is oxidized at more positive potentials to the half oxidized polyemeraldine (0.150 V) and then to the pernigraniline (1.173 V). On the reversing potential, the pernigraniline (-0.638 V) is first reduced to the polyemeraldine radical (-0.0524V) and finally to the fully reduced polyleucoemeraldine (0.069V), while the CV of indicates a pair of redox peak at (0.635, -0.856 V), with a potential peak separation ΔE_p close to 228 mV and is the lowest among the ΔE_p values observed. This confirms that the redox reaction of leucoemeraldine-emeraldine couple became more reversible on PANI-Fe₂O₃/ZnO (7%) compared to PANI-Fe₂O₃/CuO (7%). Notably, this shift and move of redox peaks process was attributed to the PANI structure changes on ZnO and Fe₂O₃ nanoparticles by preparation method, and changed its electrochemical activity.

III.5. UV-vis and Optical properties

The reflectance spectra of all the materials prepared are shown in Fig. 12. They were used to analyze the energy band gap and the nature of the electronic transitions. The absorption edges around 720 nm indicate that the products have good crystallinity [31], which is due to the direct transition of electrons and designates the material as a direct band gap material. The Kubelka-Munk diagrams for these materials are shown in Fig. 13. The reflectance diagrams clearly show that as the CuO content increases, the reflectance of the products also increases, while the reverse is true for ZnO. The extrapolation of the linear range can be used to estimate the band gap energies (E_g), as shown in Fig. 13. The optical band gap is determined by the Kubelka-Munk method [K-M or F(R)]. The K-M method is based on the following equation.

$$F(R) = (1-R)/2R \quad (1)$$

Where R is the reflectance; F(R) is proportional to the extinction coefficient (α). The basic K-M method assumes the diffuse illumination of the particulate coating [32]. A modified K-M function can be obtained by multiplying the F(R) function by hv using the corresponding coefficient (n) associated with an electronic transition as follows

$$[F(R) \times hv]^n \quad (2)$$

The band gap of semiconductor particles can be obtained by plotting this equation as a function of the photon energy in eV. In a different way, several authors applied the K-M method for calculating energy band gap (E_g). Yeredla reported the modified K-M function and plotted as [F(R) hv]² versus photon energy hv or [F(R) hv]^{1/2} versus photon energy hv. This kind of representation is known as the Tauc method [33]. The figure 11 shows the graphical representation of the modified Kubelka-Munk: photon energy hv versus [F(R) hv]². To determine the energy band gap of the obtained nanomaterials, the modified K-M function is applied. According to the Tauc plot, the value of the energy band gap for the products PANI-Fe₂O₃/CuO (3%), PANI-Fe₂O₃/CuO (5%), PANI-Fe₂O₃/ZnO (3%) and PANI-Fe₂O₃/ZnO (5%) was calculated to be 1.426 eV, 1.436 eV, 1.418 eV and 1.464 eV, respectively. It can be seen that the band gap of all products decreases with decreasing molar concentration. The change in band gap is indicative of the change in absorption of the coordinate complex formed between CuO/ZnO-Fe₂O₃ and the PANI chains, which show a decreasing trend due to the lower concentration of CuO/ZnO nanoparticles in the nanocomposites, although ZnO-based compounds outperform CuO in some cases.

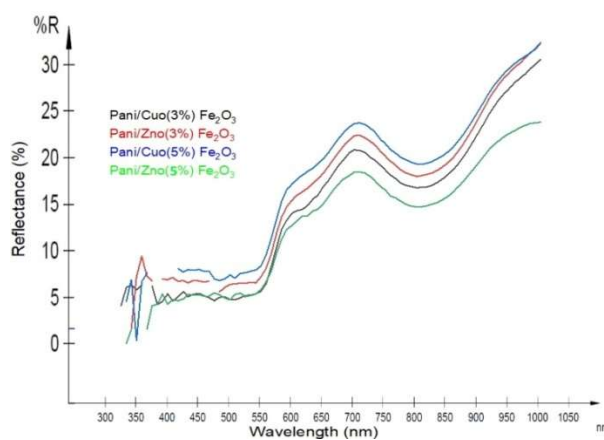


Fig. 12 UV-Vis diffuse reflectance spectrum of: PANI-Fe₂O₃/CuO (3, 5%) and PANI-Fe₂O₃/ZnO (3, 5%) nanocomposites.

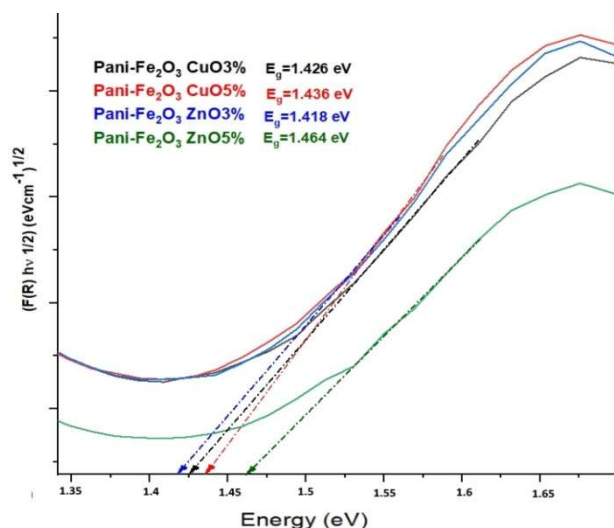


Fig. 13 Graphical representation of modified Kubelka-Munk: photon energy hv versus [F(R) hv]²

IV. CONCLUSION

A series of PANI /CuO, PANI /ZnO, PANI-Fe₂O₃/CuO, PANI-Fe₂O₃/ZnO hybrid materials with the different loading amount of ZnO and CuO (3, 5, and 7%) were prepared by In-Situ polymerization method at 0°C. The synthesized hybrid nanomaterials were analyzed by different techniques. The analyses of FT-IR, XRD, SEM and CV confirmed the formation of CuO/ZnO nanoparticles within the polyaniline matrix and proved the presence of some interaction between ferric particles and PANI. The addition of ferric oxide (Fe₂O₃) nanoparticles did not damage the backbone structure of PANI. XRD results of composites confirmed the rhombohedral (hexagonal) structures of the α -Fe₂O₃ in the amorphous structure of PANI. The XRD and SEM results approved that append of CuO/ZnO and ferric oxide results in increase of the crystallinity of hybrid materials. SEM analysis of the PANI-Fe₂O₃/ZnO-7% demonstrated different morphology to other samples, which has agglomerate, uniform and spherical grains. The electrochemical experiments showed all samples are electroactive and the ox/red properties were very important when the ZnO/CuO content is 7%. The corresponding Tauc's plots show the shift in the band gap with an increase in the concentration of CuO/ZnO in the nanocomposites. In summary, the result can clarify well that Fe₂O₃ act as significant agent. It can be referring to that specific properties can be tailored in the nanomaterials by mixing different proportions of ZnO/CuO nanoparticles. Because of these properties, the obtained nanocomposite may find application in electrical an new biological, chemical and environmental sensors.

ACKNOWLEDGMENT

This work was supported by the scientific and technical research center of physico-chemical analyzes (CRAPC), the directorate general of scientific research and technological development (DGRSDT).

FZ. Zeggai would like to thank Pr. AZZEDINE BOUSSEKSOU for his help and advice.

REFERENCES

- [1] Z. A. ALOthman, M. M. Alam, M. Naushad, & R. Bushra. Electrical conductivity and thermal stability studies on polyaniline Sn (IV) tungstomolybdate nanocomposite cation exchange material: application as Pb (II) ion-selective membrane electrode. *Int. J. Electrochem. Sci.*, vol. 10, no. 3, pp. 2663-2684, Jan. 2015, DOI: <https://dx.doi.org/10.1016/j.jiec.2014.05.022>
- [2] Z. Sun, L. Zhao, H. Wan, H. Liu, D. Wu, & X. Wang. Construction of polyaniline/carbon nanotubes-functionalized phase-change microcapsules for thermal management application of supercapacitors. *Chemical Engineering Journal*, vol. 396, pp.125317, Sep. 2020, DOI: <https://doi.org/10.1016/j.cej.2020.125317>
- [3] H. Wang, J. Lin, & Z. X. Shen. Polyaniline (PANI) based electrode materials for energy storage and conversion. *Journal of science: Advanced materials and devices*, vol. 1, no. 3, pp.225-255, Sep. 2016, DOI: <https://doi.org/10.1016/j.jsamd.2016.08.001>
- [4] Q.A. Alsulami, & A. Rajeh, A. Structural, thermal, optical characterizations of polyaniline/polymethyl methacrylate composite doped by titanium dioxide nanoparticles as an application in optoelectronic devices. *Optical Materials*, vol. 123, pp.111820, 2022, DOI: <https://doi.org/10.1016/j.optmat.2021.111820>
- [5] E. Song, & J. W. Choi. Conducting polyaniline nanowire and its applications in chemiresistive sensing. *Nanomaterials*, vol. 3, no. 3, pp.498-523, Aug. 2013, DOI: <https://doi.org/10.3390/nano3030498>
- [6] K. Crowley, M. R. Smyth, A. J. Killard, & A. Morrin. Printing polyaniline for sensor applications. *Chemical papers*, vol. 67, no. 8, pp. 771-780, Aug. 2013, DOI: <https://doi.org/10.2478/s11696-012-0301-9>
- [7] S. Sathiyarayanan, S. S. Azim, & G. J. E. A. Venkatachari. A new corrosion protection coating with polyaniline-TiO₂ composite for steel. *Electrochimica acta*, vol. 52, no. 5, pp.2068-2074, Jan. 2007, DOI: <https://doi.org/10.1016/j.electacta.2006.08.022>
- [8] P. Simon, Y. Gogotsi. Materials for electrochemical capacitors. *Nature materials*. vol. 7, no 11, pp. 845–854, Nov.2008, DOI: <https://doi.org/10.1038/nmat2297>
- [9] J. Ding, & L. Cheng. Core-shell Fe₃O₄@ SiO₂@ PANI composite: Preparation, characterization, and applications in microwave absorption. *Journal of Alloys and Compounds*, vol.881, pp. 160574, Nov. 2021, DOI: <https://doi.org/10.1016/j.jallcom.2021.160574>
- [10] J. C. Tristão, F. Magalhães, P. Corio, & M. T. C. Sansiviero. Electronic characterization and photocatalytic properties of CdS/TiO₂ semiconductor composite. *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 181, no. 2-3, pp.152-157, Jul. 2006, DOI: <https://doi.org/10.1016/j.jphotochem.2005.11.018>
- [11] N. Rahman, J. Yang, M. Sohail, R. Khan, A. Iqbal, C. Maouche, ... & A. Khan. Insight into metallic oxide semiconductor (SnO₂, ZnO, CuO, α -Fe₂O₃, WO₃)-carbon nitride (g-C₃N₄) heterojunction for gas sensing application. *Sensors and Actuators A: Physical*, vol. 332, pp. 113128, Dec. 2021, DOI: <https://doi.org/10.1016/j.sna.2021.113128>
- [12] N. Tokmoldin, N. Griffiths, D. D. Bradley, & S. A. Haque, A Hybrid Inorganic–Organic Semiconductor Light-Emitting Diode Using ZrO₂ as an Electron-Injection Layer. *Advanced Materials*, vol. 21, no. 34, pp. 3475-3478, Sep. 2009, DOI: <https://doi.org/10.1002/adma.200802594>
- [13] S. Daikh, F.Z. Zeggai, A. Bellil, A. Benyoucef. Chemical polymerization, characterization and electrochemical studies of PANI/ZnO doped with hydrochloric acid and/or zinc chloride: differences between the synthesized nanocomposites. *J. Phys. Chem. Solids* vol. 121, pp. 78–84, Oct. 2018, DOI: <https://doi.org/10.1016/j.jpcs.2018.02.003>
- [14] D. Ouis, F.Z. Zeggai, A. Belmokhtar, A. Benyoucef, B. Meddah, K. Bachari, Role of p-benzoquinone on chemically synthesized nanocomposites by polyaniline with V₂O₅ nanoparticle. *J. Inorg. Organomet. Polym. Mater.* Vol. 30, p. 3502-3510, Mar. 2020, DOI: <https://doi.org/10.1007/s10904-020-01508-7>
- [15] B.K. Sharma, A.K. Gupta, N. Khare, S.K. Dhawan, H.C. Gupta, Synthesis and characterization of polyaniline-ZnO composite and its dielectric behavior, *Synth. Met.* Vol. 159, no. 5-6, pp. 391–395, Mar. 2009, DOI: <https://doi.org/10.1016/j.synthmet.2008.10.010>
- [16] T.K. Sarma, A. Chattopadhyay, Reversible encapsulation of nanometer-size polyaniline and polyaniline-Au-nanoparticle composite in starch, *Langmuir*, vol. 20, no. 11, pp. 4733–4737, Apr. 2004, DOI: <https://doi.org/10.1021/la0495884>
- [17] G.K. Paul, A. Bhaumik, A.S. Patra, S.K. Bera, Enhanced photo-electric response of ZnO/polyaniline layer-by-layer self-assembled films, *Mater. Chem. Phys.* vol. 106, no 2-3, pp. 360-363, Dec. 2007, DOI: <https://doi.org/10.1016/j.matchemphys.2007.06.013>
- [18] Z. Zhang, X. Li, C. Wang, L. Wei, Y. Liu, C. Shao. ZnO hollow nanofibers: fabrication from facile single capillary electrospinning and applications in gas sensors. *The Journal of Physical Chemistry C*, vol. 113, no 45, pp. 19397-19403, Oct. 2009, DOI: <https://doi.org/10.1021/jp9070373>
- [19] N. Samaele, P. Amornpitoksuk, S. Suwanboon, Effect of pH on the morphology and optical properties of modified ZnO particles by SDS via a precipitation method, *Powder Technol.* vol. 203, no 2, pp. 243-247, Nov. 2010, DOI: <https://doi.org/10.1016/j.powtec.2010.05.014>
- [20] V. Prasad, C. D'Souza, D. Yadav, A.J. Shaikh, N. Vigneshwaran, Spectroscopic characterization of zinc oxide nanorods synthesized by solid-state reaction, *Spectrochim. Acta A Mol. Spectros* vol. 65, no. 1, pp. 173–178, Sep. 2006, DOI: <https://doi.org/10.1016/j.saa.2005.10.001>
- [21] M. Nagaraja, S. Prashanth, J. Pattar, H. M. Mahesh, & K. Rajanna. Polyaniline-CuO nanocomposite: Electrical, structural and sensor properties. *Materials Today: Proceedings*, vol. 49, pp. 1989-1992, Aug. 2021, DOI: <https://doi.org/10.1016/j.matpr.2021.08.154>
- [22] A. Olad, & H. Rasouli. Enhanced corrosion protective coating based on conducting polyaniline/zinc nanocomposite. *Journal of applied polymer science*, vol. 115, no. 4, pp. 2221-2227, 2010, DOI: <https://doi.org/10.1002/app.31320>
- [23] S. S. Umare, & B. H. Shambharkar. Synthesis, characterization, and corrosion inhibition study of polyaniline- α -Fe₂O₃ nanocomposite. *Journal of applied polymer science*, vol. 127, no. 5, pp. 3349-3355, May. 2013, DOI: <https://doi.org/10.1002/app.37799>
- [24] L. Shi, X. Wang, L. Lu, X. Yang, X. Wu. Preparation of TiO₂/polyaniline nanocomposite from a lyotropic liquid crystalline solution, *Synthetic Metals* vol. 159, no. 23-24, pp. 2525–2529, Dec. 2009m DOI: <https://doi.org/10.1016/j.synthmet.2009.08.056>
- [25] M. Guo, P. Diao, and S. Cai. Hydrothermal Growth of Well-Aligned ZnO Nanorod Arrays: Dependence of Morphology and Alignment Ordering upon Preparing Conditions. *Journal of Solid State Chemistry*, vol. 178, no. 6, pp. 1864-1873, Jun. 2005, DOI: <https://doi.org/10.1016/j.jssc.2005.03.031>
- [26] F. Bigdeli, A. Morsali, and P. Retalleau. Synthesis and Characterization of Different zinc (II) Oxide Nano-Structures from Direct Thermal Decomposition of ID Coordination Polymers. *Polyhedron*, vol. 29, no. 2, pp. 801-806, Feb. 2010, DOI: <https://doi.org/10.1016/j.poly.2009.10.027>

- [27] J. Wang, S. He, Z. Li, X. Jing, M. Zhang, Z. Jiang. Synthesis of chrysalis-like CuO nanocrystals and their catalytic activity in the thermal decomposition of ammonium perchlorate. *J Chem Sci* vol. 121, no. 6, pp. 1077–1081, Nov. 2009, DOI: <https://doi.org/10.1007/s12039-009-0122-8>
- [28] L. E. Mathevela, L. L. Notoa, B. M. Mothudia, M. Chithambob, M.S. Dhlamini. Structural and optical properties of sol-gel derived α -Fe₂O₃ nanoparticles. *Journal of Luminescence*. Vol. 192, pp. 879–887, Dec. 2017, DOI: <https://doi.org/10.1016/j.jlumin.2017.07.055>
- [29] A. Gok and S. Sen, GÖK. Preparation and characterization of poly (2-chloroaniline)/SiO₂ nanocomposite via oxidative polymerization: Comparative UV–vis studies into different solvents of poly (2-chloroaniline) and poly (2-chloroaniline)/SiO₂. *Journal of applied polymer science*, vol. 102, no 1, pp. 935-943, Jul. 2006, DOI: <https://doi.org/10.1002/app.24266>
- [30] G. D. Khuspe, S. T. Navale, D. K. Bandgar, R. D. Sakhare, M. A. Chougule, B. SnO₂ nanoparticles-modified polyaniline films as highly selective, sensitive, reproducible and stable ammonia sensors. *Electronic Materials Letters*, vol. 10, pp. 191-197, Jan. 2014, DOI: <https://doi.org/10.1007/s13391-013-3096-0>
- [31] T. T. Lun, C. Q. Liu, N. Wang, X. N. Zhai, M. S. Song, Q. Ge, X. Y. Zhan, S. M. Liu, H. L. Wang, W. W. Jiang, W. Y. Ding. Preparation of compact CuO films by sol-gel spin coating technique. *Materials Letters*, vol. 257, pp. 126745, Dec. 2019, DOI: <https://doi.org/10.1016/j.matlet.2019.126745>
- [32] P. Kubelka, F. Munk. An article on optics of paint layers. *Zeitschrift für Technische Physik*, vol. 12, no 593-601, pp. 259-274, Aug. 1931, See also English translation by S. Westin (An article on optics of paint layers, <http://www.graphics.cornell.edu/~westin/pubs/kubelka.pdf>)
- [33] R.R. Yeredla, H. Xu. An investigation of nanostructured rutile and anatase plates for improving the photosplitting of water. *Nanotechnology*, vol. 19, no. 5, pp. 055706, Jan. 2008, DOI: 10.1088/0957-4484/19/05/055706



Fatima Zohra Zeggai, born on 24-09-1988 in Mascara, is a PhD scientist at CRAPC research centre in Tipaza – Algeria, a member of the Polymer Chemistry Laboratory – University of Ahmed Ben-Bella Oran1 and an ambassador of Africa Elsevier Algeria. She holds a PhD in Materials Chemistry

and Environment from Mustapha Stambouli-Mascara University. She is a member of the department of oxides and porous materials at CRAPC. For years, her interest is focused on materials chemistry (nanomaterials, nanoparticles, carbon materials, conducting polymers, mesoporous materials, pyrochlore), published in many prestigious international journals.

Behavior of Materials in the Presence of Particles Additive Technique: A Review

Fares Mohammed Laid Rekbi

Abstract– Recently, engineers and researchers have been concerned about how to improve the behavior of materials used in manufacturing. Ensuring the compatibility of particle, as main constituents with other reinforcement, in composites for specific behavior is essential. In this review, we attempt to list the salient features of experimental as well as numerical investigation on characteristics composite materials with adding either micro- or nano-particles, which is one of the ways to express it. The behavior of composites materials such as mechanical enhanced with different form, size, type and nature of particle additives. The bibliography review concludes that it would be important to investigate extensively the features of this technique in order to get more discoveries and developments of materials experimentally and numerically. Some contributions have identified the research gaps and deduced that the potential application of particles as additive agents in composites have not been more explored.

Keywords– Particles, Nanocomposites, Composite Materials, Behavior.

NOMENCLATURE

PP	Polypropylene.
NPs	Nanoparticles.
MWCNT	Multi-walled carbon nanotubes.
TSP	Tamarind seeds powder.
NS	Nanosilica.
GNPs	Graphene nanoplatelets.
FWP	Filament winding pipes.
CSR	Core-shell rubber.
LVI	Low- velocity Impact.
HVI	High- velocity Impact.
SEM	Scanning electronic microscopy.
IT	Infrared thermography.
FMLs	Fibers metal laminates.
CFRP	Carbon fiber reinforced pipe.
GF-SMC	Glass fiber sheet molding.
NFRBC	Natural fiber reinforced biocomposite.
NFRP	Natural fiber reinforced polymer.
MAPP	Malcated polypropylene.
Phc	Per hundred compounds.
NDT	Nondestructive testing.

I. INTRODUCTION

The researchers are interested in improving the properties of materials where this provides potential opportunities to create better industrial and sustainable materials for use in several application fields. For example, Lee Byoung-Ho et al. [1] demonstrated that the breaking strain and tensile strength of

natural fiber reinforced composites becomes lower than that of the pure PP matrix, this can be explained by both voids and the interfacial adhesion fiber/matrix in the composites. These reasons make engineers to find solutions to them, such as nano or macro particle additions. It has led to great and growing interest, both in academia and industry area. To achieve the desired technical effect in the final composite, what is known as an additive is used, which is incorporated into the materials to become an essential part of the final material. Composite material reinforced with nano particles, also named nanocomposites are being investigated worldwide in recent years. Generally These types of materials produce with mixture of most than two materials producing new material with the nano range dimension [2]. And by incorporation of the particle are on a weight basis for the advanced composite[3]. From Mohajerani Abbas et al. [4] and Venkatesh Nagasarny et al. [5] particles sized in dimensions (diameter, with, length and thickness) range of 1 up to 100 nanometres and ultrafine are defined nanoparticle. The nanoparticles (NPs) also are defined as the combination of molecules or atoms up to millions and are frequently named simply clusters or nano clusters from theoretical point view [6]. Venkatesh Nagasarny et al. [5] noted that the metallic nanoparticle is important because of their ideal optical, magnetic, electrical and chemical properties. The NPs could be seen in the nanotube, particles and powder forms, etc. such as clay, carbon nano-powder and carbon nano-tubes which are the widely used nano-particles [7]. The table 1 is summarized the class of NPs which are to organic and inorganic in nature [8].

Table. I

EXAMPLE OF NANOPARTICLES NATURE

Organic	Inorganic
Coir nanofiller	Silica (SiO ₂)
Carbon black	Titanium dioxide (TiO ₂)
Cellulosic nanofiller	Calcium carbonate (CaCO ₃)
Natural particles, etc.	Polyhedral oligomeric silsesquioxane (POSS), etc.

The huge number of applications of nanocomposites is in great and continuous growing at faster rate these days, in engineering, medicine and Ultraviolet protection gels and anti-corrosion barrier protection ... etc.[2], [9]. The use of nanoparticles reinforced polymer matrix composite

Manuscript received September 21, 2022; revised April 13, 2023.

Fares Mohammed Laid REKBI is with Research Center in Industrial Technologies (CRTI), P. O. Box 64, Cheraga 16014, Algiers, Algeria. (Email: f.rekbi@crti.dz)

materials (Fig. 1) in engineering application is increasing due to their high strength/stiffness to low weight ratio, corrosion resistance, ease of fabrication economically efficient properties and environmentally friendly [10].

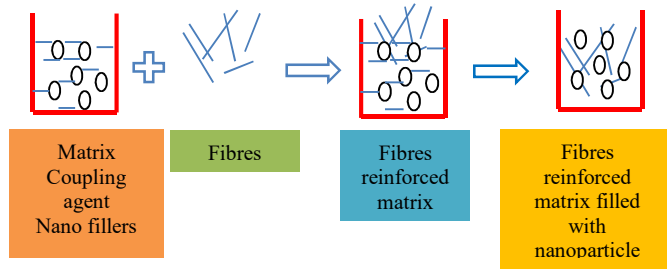


Fig. 1: Formation of fiber reinforced matrix filled with nanoparticle.

One of the challenge fields that a more study has been carried out about them is adding the nanoparticle such as (SiO_2) [11]-[12], nanosilica [13]-[14], nanoclay [15]-[16], grapheme [17] and grapheme oxide and nanozirconia [18], titanium dioxide (TiO_2) [19]-[20], matrix filled with cork powder [21], Tamarind seeds (TSP) powder [22] into the composite materials. The incorporation of the particle by dispersed it in the matrix (Fig. 1) [11], coated the fibers (Fig. 2) [23] or a direct addition of particle into composite [24]. Very often, homogeneous distribution of the nanosized particles is problematic and aggregation phenomena is a major subject in composite materials having spherical nanoparticles [3].

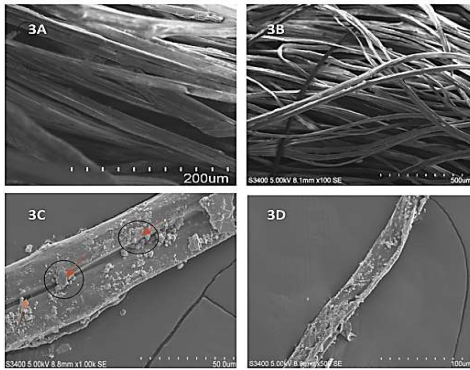


Fig. 2: SEM observaion (a) and (b) uncoated silk fibers, (c) and (d) SnO coated silk fibers with uniform distribution of nanoparticles [32].

Recently several papers appear on reinforced composite with particles additive based nano or macro particle, with limited attention on different behaviors and which parameters influenced it that. For example, Shalwan A and Yousif B F [25] noted that the mechanical and tribological performance of date palm fiber/epoxy reinforced composites DPFERCs get improved by graphite particle additive but high weight of it deteriorates the mechanical behaviors. The essential aim of this study focus on the more understands on the parameters influenced on the behaviors of these materials.

II. APPLICATIONS OF THE NANOCOMPOSITE MATERIALS

For example, the optimizing and improvement of physical properties of functional nanocomposites allow new application e.g., in electronics, microoptics, energy conversion or storage [26]. Metallic nanoparticles give wide range of application in therapeutic, vehicles for gene and biotechnology [5]. In what follows the most potential use in construction are presented. The expected benefits of carbon nanotubes are mechanical durability and crack prevention in concrete makes it competitive for use in construction application materials. Also, the titanium dioxide nanoparticles TiO_2 are added to concrete to improve its properties, is used as an excellent reflective coating added to paints, cements and

windows for its sterilizing properties [27]. In addition to all these construction applications may find the nao-SiO_2 used for increase the compressive strength of concretes by filling the pores. In addition to applications, Wu Yingji et al. [28] proved the possibility of a new nanocomposite material for automotive applications based on ZnO particle addition. Presting H and Konig U [29] noted that the automotive industry is diverse or manifold with the application on nanotechnology by used of nanocomposite materials. Also, to fluid transportation application, Di Chengrui [12] demonstrated that the used of additives on the filament winding structures for this application to produce part such as pipe or tube. The use of nano material fiber composites in fields of intelligent communication, barrier packaging and higher value printing also addressed in study of Kamel S [30] he noted that the paper and pulp industry is a material which gives an excellent fields for developing nanomaterials. Abd-Okail Mohamed et al. [31] investigated in the one of the recent vital area used in renewable energy field is wind energy. They confirmed the possibility to fabricate wind turbine blade is used to generate energy with addition the nanoparticle in the based composites materials.

III. WHY PARTICLES ADDITION?

- Fiber surface modification: the chemical inert properties of carbon fibers surface lead to weak interfacial adhesion fibre/resin [33]-[34].
- Hydrophilic and hydrophobic nature: the hydrophilic property of natural fiber lead to weak interfacial adhesion fibre/matrix [8].

IV. NANOCOMPOSITE BEHAVIOR

Nowadays, a great deal of researches and papers are in deployment towards more particles to produce a huge variety of nanocomposites. Table 2 listed works on nanocomposites and technology of particles with different scale regarding several fiber/matrix systems, in addition to various including (pipe, laminate, Prosthetic composite and biaxial braider, etc.). Also, to various architectures of fiber (Unidirectional, Long, Short or Weave, etc.), (Synthetic or Natural) and to system of reinforcement (Hybrid or Nohybrid). This addition of particles may be nano as previously mentioned or micro size [38]. Fu Shao-Yun et al. [42] show that are strongly effect of particle size, particle/matrix and particle loading on composite materials toughness and strength, especially particle/matrix adhesion factor. From literatures, Ebrahimnezhad Khaljiri et al. [15] declared that the main objective for adding particles is enhancing and improving the mechanical behaviors of composites, enhancing fiber matrix interfacial [18]-[11] and to make composites could withstand high impact load and improve strength of laminates [7]. Also, improvement the properties of composites such as physical and thermal properties [8]. To increase the surface roughness on case of natural fiber which to provide an additional region for interlocking along with matrix with the chemical bond formations [43]-[19]. So, there is a various contributions by researchers have been conducted to understand the properties of composite materials, these studies included tensile, flexural and impact etc. tests carried out for particles effect on their behavior (Table 3). They observed that are effective improvement on mechanical properties in the case of nanolayers clay addition and that when the polymer is in its rubbery state versus the glassy state, also the dimensional stability, solvent resistance and thermal stability of the glassy matrix can also be increased [10].

Table. II
REPORTED RESEARCH ON EFFECT OF PARTICLE ON COMPOSITES PROPERTIES

Material	Structure	Addition	Size/ weight	Test	Key funding	Refs.
E glass/Epoxy	Sandwich	Graphene nanoparticule	An outer diameter and thickness of 10-20nm / 0.1%, 0.3% and 0.5% of weight	Tensile	The effect the weight addition of nanoparticle on the tensile strength	[17]
Carbon/Epoxy	Pipe	Multi-walled carbon nanotubes (MWCNT)	/	Impact	Impact behavior of filament winding pipes at cryogenic temperatures	[35]
Carbon/Epoxy	Tube	Nanosilica particles	15 and 25 weight percent in epoxy	Ballistic impact	Incorporation effect of variable amounts of nanosilica (NS) in the matrix	[13]
Glass/Epoxy	Laminate	Micro (nanoclay) and nano (micro-Glass Bubbles)	Nanoclay (6 μ m) Glass Bubbles 20 μ m/ 1wt.% weight content	Drop-weight impact	Effect of hybrid from micro and nano fillers additive on impact behavior composite	[36]
Carbon/Epoxy	Pipe	Core-shell rubber (CSR) nanoparticle and nano-SiO ₂ rigid particles	/	Tensile, flexural and impact	Effect of addition mechanical behavior of resin and composites	[12]
Carbon/Epoxy	Laminate	Nano-SiO ₂	1-8wt.% weight	Low- velocity Impact	SiO ₂ nanoparticle effect on impact damage size, flexural strength and impact resistance	[11]
Aluminum-Jute/ Epoxy	Fiber metal laminate (FML)	Nanoclay	0, 1, 3 and 5wt.%	High-velocity impact	Nanoclay particles effect on the impact response of composite	[15]
Basalt/Epoxy	Laminate	Graphene oxide and nanozirconia	0.1- 0.3wt.% graphing oxide and 1-3wt.% nanozirconia	Three point bending test and Dry-sliding wear	Flexural and tribological properties when add grapheme and nanozirconia particles	[18]
Carbon/Epoxy	Laminate	Silica nanoparticles	/	fatigue and Mode I interlaminar fracture	Effect of fiber modification with nanoparticle on the toughness of composites	[14]
Flax/Epoxy	Laminate	Nano TiO ₂	0.2wt.% -2wt.%	Tensile, flexural and Water absorption	Effect of fiber coating by nanoparticle on mechanical properties of composite	[23]
Perlon /Kevlar/ Glass	Prosthetic composite materials	Nano AL ₂ O ₃ and SiO ₂	0-2% volume fraction	Tensile and fatigue	Effect of volume fraction (V_f) of nanoparticle on fatigue property of composites	[37]
Kenaf/polyester matrix	Composite for automotive application	ZnO	5.9, 12.4 and 18.9wt.%	Tensile, 3-points flexural and water absorption	Effect of ZnO nanoparticle on developing a natural reinforced composites to replace GF-SMC	[28]
Carbon/Epoxy	Flat biaxial braided composite	TiO ₂	0 to 5wt.%	Impact, flexural and tensile	Evaluation the effect of nanoparticle addition on mechanical properties of braided composite materials	[20]
Plain weave Carbon/Epoxy	Laminate	Silica nanoparticle and silica microparticle	1 and 3.5wt.%	Tensile and impact	The effect of nano and micro silica particle on impact resistance of composite	[38]
Kevlar and Carbon/Epoxy	Laminate	Cork powder	/	Static bending test	Effect of introduce cork powder in matrix on behavior of composite	[21]
Flax/Thermoplastic matrix	Laminate	Tamarind seeds powder (TSP)	5 to 15% of the weight of the matrix	Tensile, bending and moisture absorption	Influence of new developed natural additive material on composites behavior	[22]
Unidirectional E-Glass/polypropylene (PP)	Pultrude composite beam	Nanoclay	0-5 wt.% and 10 wt.%	Compression	Effect of nanoparticle content and pultusion manufacturing process variable on the mechanical properties	[39]

Glass/Vinyl ester	/	Nanoclay	0, 1, 3 and 5wt.%	Free vibration	Effect of additive on vibration characteristics	[40]
Rice husk flour/polyethylene (HDPE)	Injection molding composites	Nanoclay	0, 2, 4 and 6wt.%	Tensile and thermal	Nanofiller addition effect on the thermal behavior and rheological response	[41]
Reed/polypropylene	Injection molding composites	Nanoclay	0, 2 and 4wt.%	Water absorption and tensile	Evaluation the effect of nanoclay particle on mechanical and physical characteristics of the nanocomposite	[16]
Carbon/Glass/Epoxy	Wind turbines blade	Alumina nanoparticle (Al_2O_3) and graphene nanoplatelets (GNPs)	1.5wt.% Al_2O_3 +1.5wt.% GNPs And 3wt.% Al_2O_3	Tensile, flexural and hardness	Effect of the dispersion of nanoparticle on microstructure, tensile strength, bending strength and hardness	[31]
Wood flour/HDPE	/	Nanoclay	/	Flexural, tensile and dynamic	Effect of two approach of incorporation of nanoparticle on mechanical properties	[24]

The results of this study show also the damage type on composite (Fig. 3) and the effect of nano particle additive on strength of layered composite structures (Fig. 4), where observed the amount of 0.1% and 0.3% nanoparticle graphene additive led to 9% up to 22% increase in the composite strength. Also, an optimum graphene amount exists in the composites structure and excess amount weight of graphene nanoparticle additive caused a decrease in the strength of composite structures. Through all these observations was found optimum amount graphene additive to be 0.1wt.% and composites was significantly influenced by graphene nanoparticles.

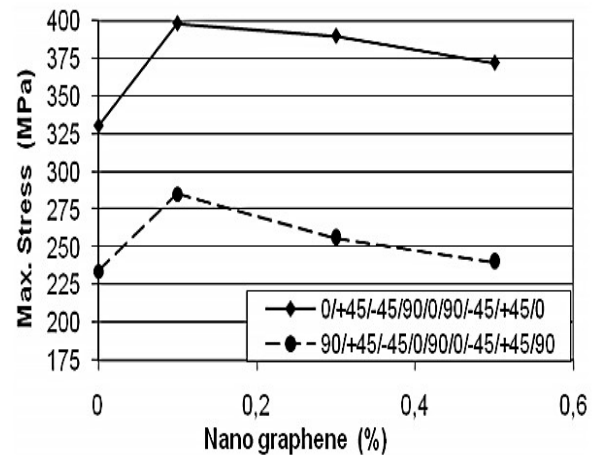


Fig. 4 : Nano particle weight effect on the tensile strength [17].

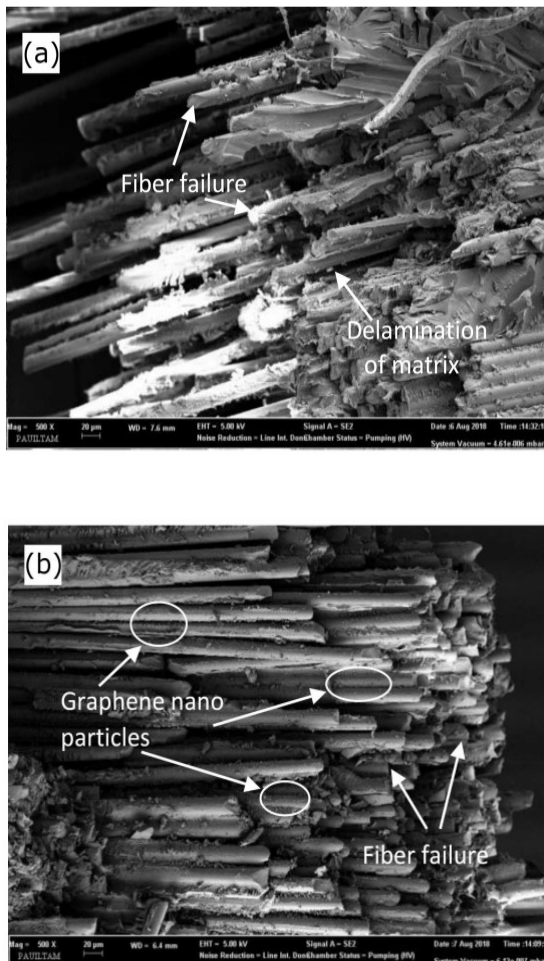


Fig. 3 : Fracture zone SEM observation (a) absence of graphene nanoparticle, (b) presence of nanoparticle additive [17].

Aniruddh Vashisth et al. [13] in their experimental investigation on impact of carbon/epoxy tubes loaded in torsion show that when the addition of nanosilica (NS) decreased of the impact damage area by 50%, increased the energy absorbed per unit damage area by 120 and increased the residual shear strength by 38% compared to the material with no NS. While in overall, the incorporation of NS significantly improved the impact tolerance of carbon/epoxy tubes loaded in torsion test, with little change in the glass transition temperature, mass density and elastic modulus. The additive hybridization effect on behavior of composites laminate was performed by Ermias G Koricho et al. [36], two fillers (nano- and micro) chosen were utilized in their study. The result of visual inspection show that the evolution on the stiffness and peak force with varying energy levels and show that Glass Bubble modified composite laminates are characterized the lower absorbed energy and high peak force with penetration of the impactor through their thickness at high impact energy levels (262J) (Fig. 5). While nanoclay modified composite laminates are characterized by highest absorbed energy, the minimum peak reaction force and without penetration of impactor. But in the case of hybrid modified composites laminates exhibited intermediate absorbed energy and peak reaction force sustained for longer time (Fig. 6).

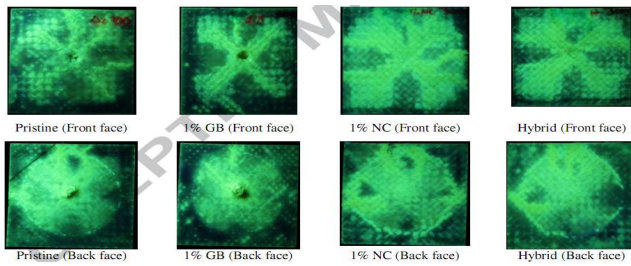


Fig. 5: Evaluation of post-impact by dye penetration method at 260J, Comparison images [36].

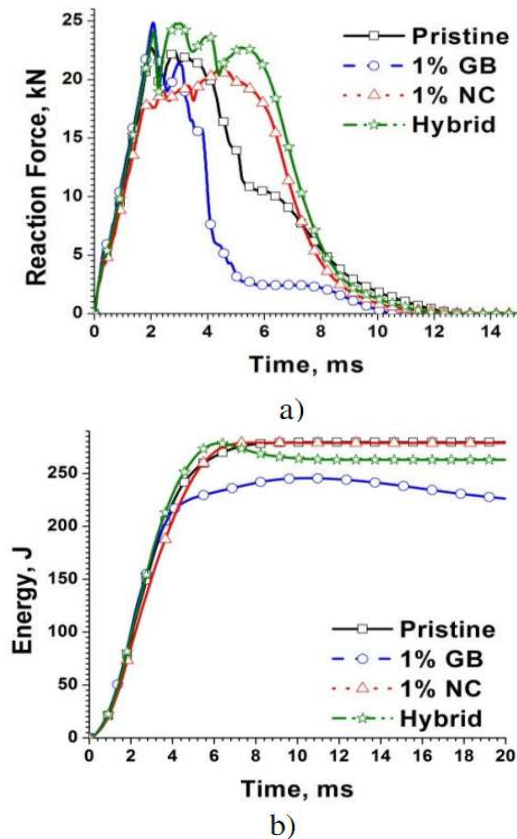


Fig. 6: a) Reaction force-time, b) Energy-time at 262J comparison of material behavior [36].

The experimental investigation of Di Chengrui et al. [12] demonstrated that modified epoxy matrix enhanced the mechanical behavior of carbon/epoxy reinforced wound composites pipes, the Young's modulus, interlaminar shear strength and tensile strength were enhanced by 4.56%, 18.9% and 14.0%, respectively, compared with the composites pipe based on unmodified matrix. The authors also mentioned that the preparation process is simple because the resin system is low, so it is of practical implication to market application. Which is highlighted by the SEM observations when shown the fiber was tightly coated by resin, which suggested that the modified resin exhibited a better interface with the fiber (Fig. 7).

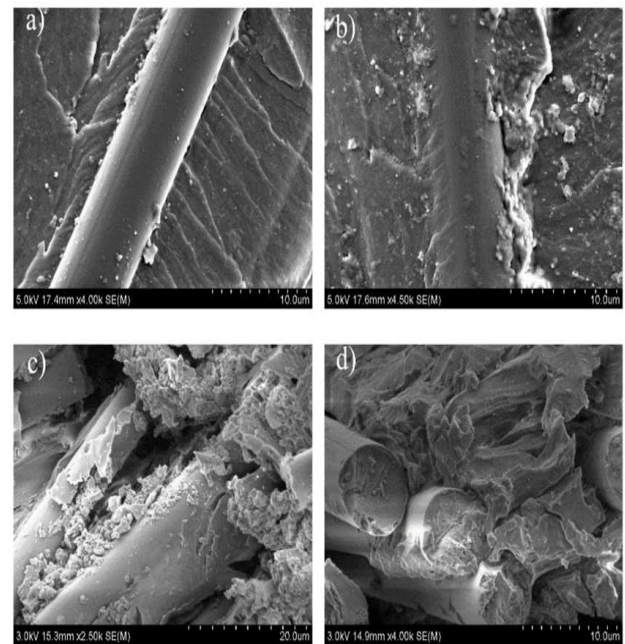
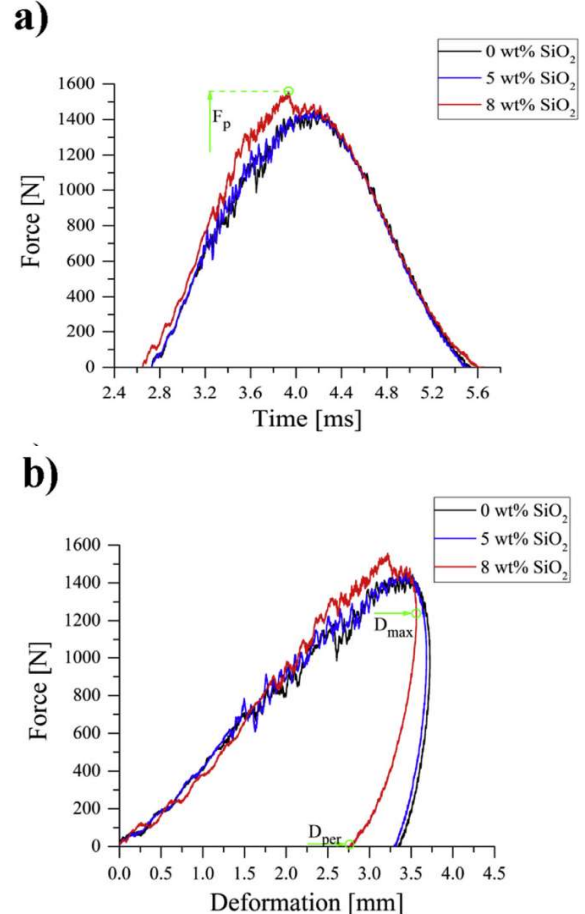


Fig. 7: SEM images of composite materials (a and b) of interlaminar shearfailure surface, (c and d) of tensile fracture surface [12].

Landowski Michal et al. [11] demonstrated the effect of SiO_2 nanoparticle on flexural behavior, impact resistance and impact damage size. As a result of the study, they are seen that the SiO_2 nanoparticle addition make significant influence on mechanical behavior of carbon/epoxy composite laminates, especially in term of impact damage behavior. Where these results in 3 parameter terms: absorbed energy (E_a), a peak impact force (F_p) and permanent deformation (D_{per}) (Fig. 8).



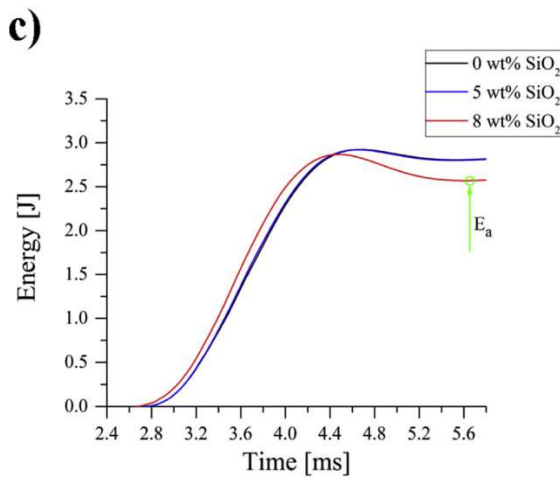


Fig. 8: a) force-time, b) Force-deformation, c) Energy-time for 0, 5 and 8wt.% SiO₂ at impact tests [11].

Also, by nondestructive evaluation via infrared thermography method (IT) (Fig. 9) the impact damage results for the different weight percent of SiO₂ nanoparticle (0, 5, and 8%) were illustrated, the authors concluded that from this analysis diminution of the damage area with increasing nanoparticle content. Also, it was observed a transition in properties of SiO₂ peak strength at 5% and initiation of decrease in impact damage size associated with energy absorbing mechanisms of crack branching and crack deflection due to nanoparticle agglomerates phenomenon.

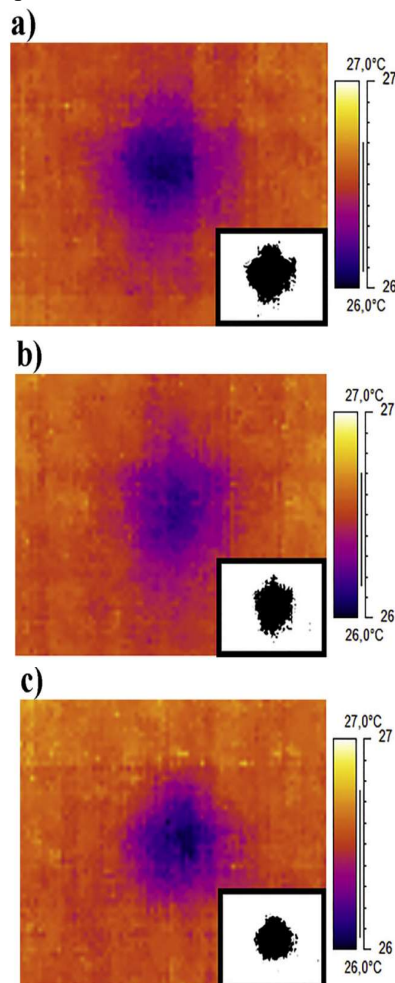


Fig. 9: Infrared thermography images of impact damage area, a) 0%, b) 5% and c) 8% of SiO₂ nanoparticle [11].

In another one part study carried out by Ebrahimnezhad-Khaljiri Hossein et al. [15] the nanoclay particle with various percentages (0, 1, 3 and 5wt.%) effect on the impact response

of fibers metal laminates (FMLs) from aluminum-Jute fiber and epoxy matrix was investigated. The results of the study showed that the incorporation of nanoclay was effective in formation of the limited velocity energy, absorbed energy (Fig. 10), damage area (Fig. 11) and delamination length (Fig. 12).

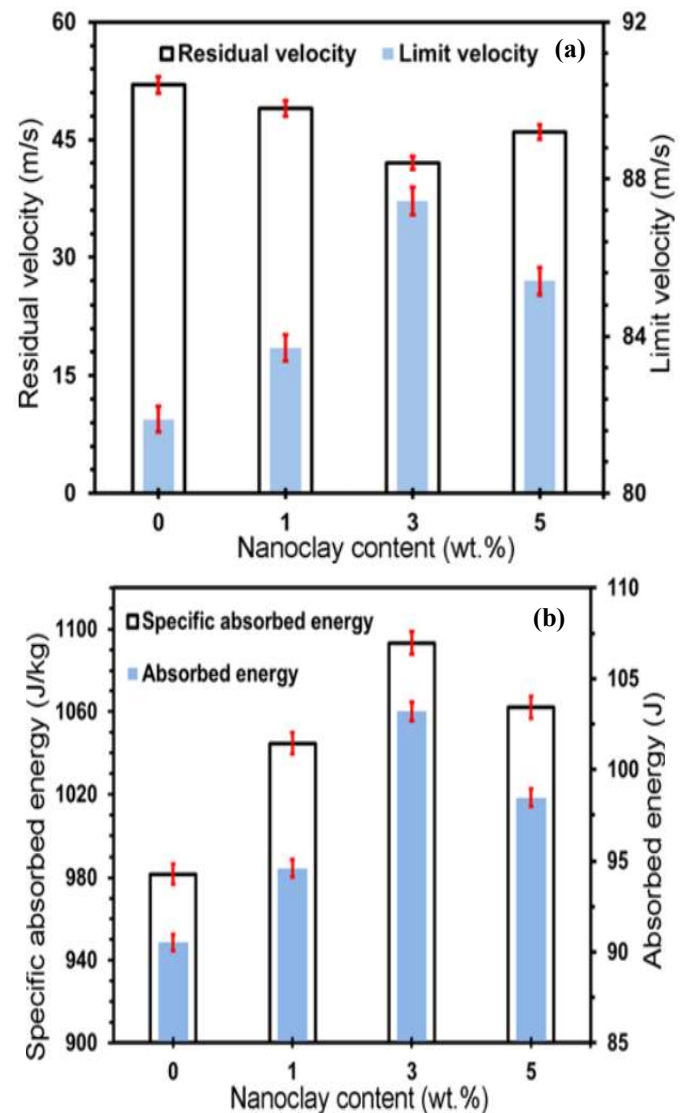


Fig. 10: FMLs impact results (a) limit velocity impact and the residual velocity, (b) the specific absorbed energy and absorbed energy [15].

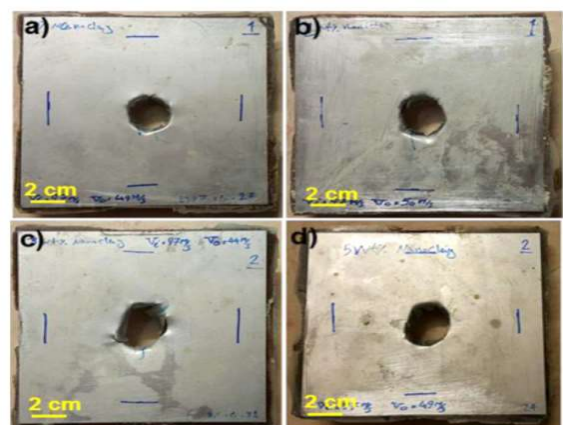


Fig. 11: Photographs of damage area in FMLs with nanoclay 0wt.%, 1wt.%, 3wt.% and 5wt.% of a), b), c), d), respectively. [15].

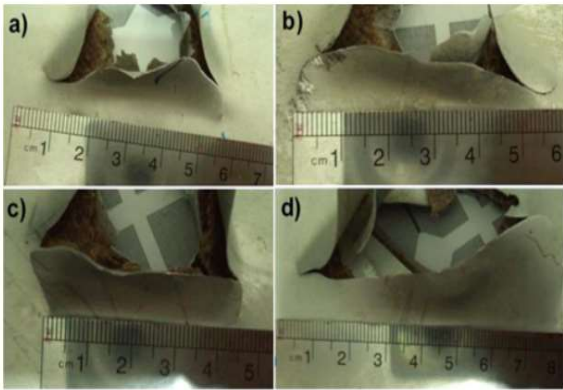


Fig. 12: Images of delamination length in the fibers metal laminates with nanoclay 0wt.%, 1wt.%, 3wt.% and 5wt.% of a), b), c), d), respectively. [15].

In this study the nanoparticle weight percent effect was been addressed and analyzed, where observed the higher impact properties on case of the FMLs with the 3 wt.% nanoclay when compared with the other laminates. The limited velocity reached to 87m/s, 103.2J absorbed energy, 7.6cm damaged area and 1093J/kg specific absorbed energy. The authors noted that the effect of nanoclay on the improvement of adhesion between aluminum layer and composite core led to minimum delamination length (Fig. 13). From Fig. 13(a), it observed that the adhesion fiber/resin is weak because the epoxy resin cannot be seen on the Jute fibers surface. The authors returned this reason to the hydrophilic nature of the natural Jute fibers led to effect on the mechanical properties of the materials. But the authors noted that adhesion between fibers and resin was improved when addition of nanoclay into the matrix from 1 up to 3wt.% which can be observed in figure Fig. 13(b) and Fig. 13(c). In the case of 5wt.% nanoclay addition, they were seen the adhesion between matrix and fiber has been reduced Fig. 13(d).

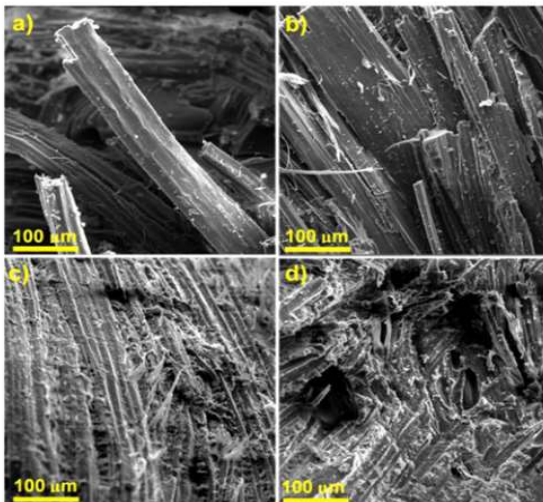


Fig. 13: Fracture surface of FMLs after high-velocity impact test with nanoclay, a) 0, b) 1, c) 3 and d) 5wt.%, SEM images [15].

Also, concerned the conclusions of this investigation the authors mentioned a phenomenon characterized the natural fiber, which is the fibrillation phenomenon (Fig. 14) helps to absorbed the energy in composite materials.

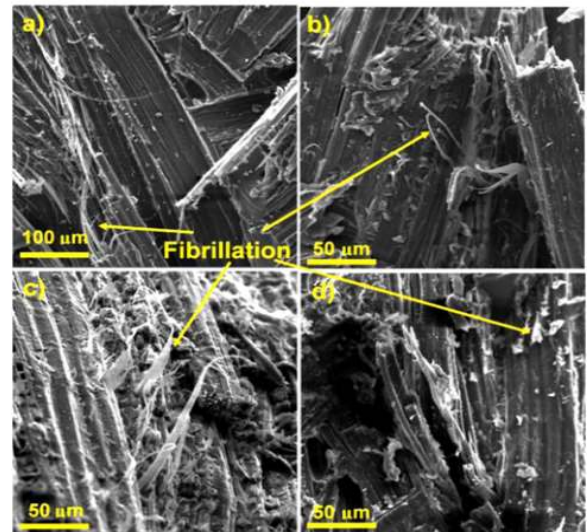


Fig. 14: Fibrillation phenomenon of Jute fibers, a) 0, b) 1, c) 3 and d) 5wt.%, SEM images [15].

The Fig. 14(a) show the fibrillation of the jute fibers is very low by addition of 1wt.% nanoclay. Where observed this phenomenon increased up to maximum value belongs to the laminates containing 3wt.% nanoclay particle (seen Fig. 14(b) and (c)). Also, the Fig. 14(d) shown the reduced of the Jut fibers fibrillation compared with the 1 and 3wt.% nanoclay composites. These led to declare that 3wt.% is the optimum percentage of nanoclay addition. Davood Toorchi at al. [18] were used the additive alone and by hybridation in their work, by using the graphene oxide and nano-zirconia. In this study, the laminate composites with various amount (0.1, 0.3 and 0.5wt.%) and (1, 2 and 3wt.%) of graphene-oxide and, nanozirconia, respectively. or hybrid system from graphene-oxide/nanozirconia in the resin were manufactured, their tribological property and flexural behavior were investigated under dry-sliding wear and three point bending, respectively. The results show that graphene-oxide loaded sample with the 0.3wt.% filler content demonstrated the maximum improvement up to 33% in flexural strength property, while for nanozirconia particle enhanced laminates, the highest flexural strength shown in the specimen with 1wt.% nanozirconia by increasing up to 29% . Also, the positive effect of nanohybrid system of additive on flexural strength is observed specially when hybridization of 0.1wt.% graphene oxide with 1wt.% nanozirconia which increasing up to 50% (Fig. 15). All these results due to enhance of fiber-matrix interfacial. However, the authors declared that the the flexural strength of laminates is declined probably in the case of hybridization of higher loading content on nanofilles (3wt.% nanozirconia and 0.5wt.% graphene oxide), due to the formation of nanofiller agglomerates phenomenon within the interface or matrix (Fig. 16).

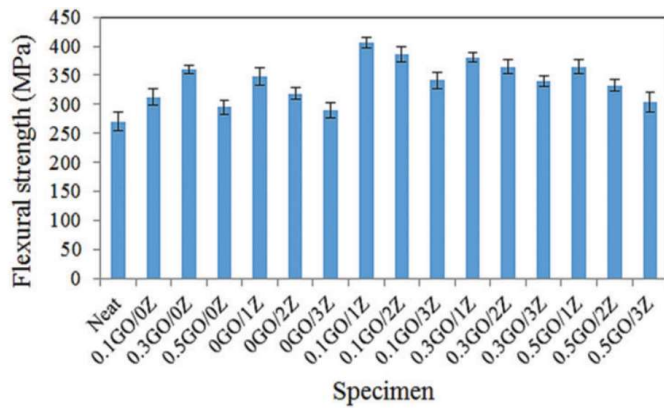


Fig. 15: The variation results of flexural strength values Vs. addition content [18].

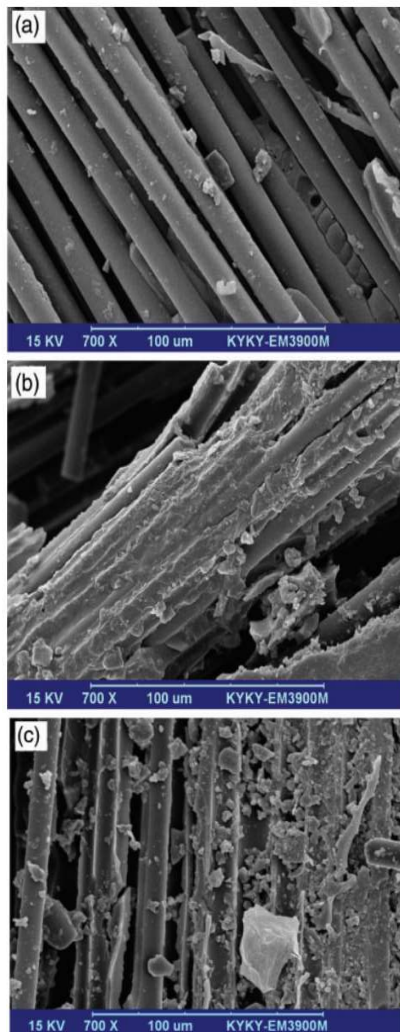


Fig. 16: SEM images of fracture surface images (a), (b) and (c) neat basalt fiber-epoxy laminate, multiscale 0.1wt.% graphene oxide plus 1wt.% nanozirconia-enhanced sample and multiscale 0.5wt.% graphene oxide plus 3wt.% nanozirconia- enhanced sample, respectively. [18].

The results of the tribological analysis show the stats of the surface and damage mechanisms. The matrix cracking, fiber/matrix debonding and fiber breakage observed on the worn surface of the neat basalt/epoxy laminate Fig. 17(a). But the addition of nanofilles enhancing of interfacial between matrix and basalt fibers and the laminate has a smooth surface Fig. 17(b). However, roughness surface for the laminate composites for the worn surface of multiscale 0.5wt.% graphene oxide + 3wt.% nanozirconia filled basalt/epoxy composite Fig. 17(c).

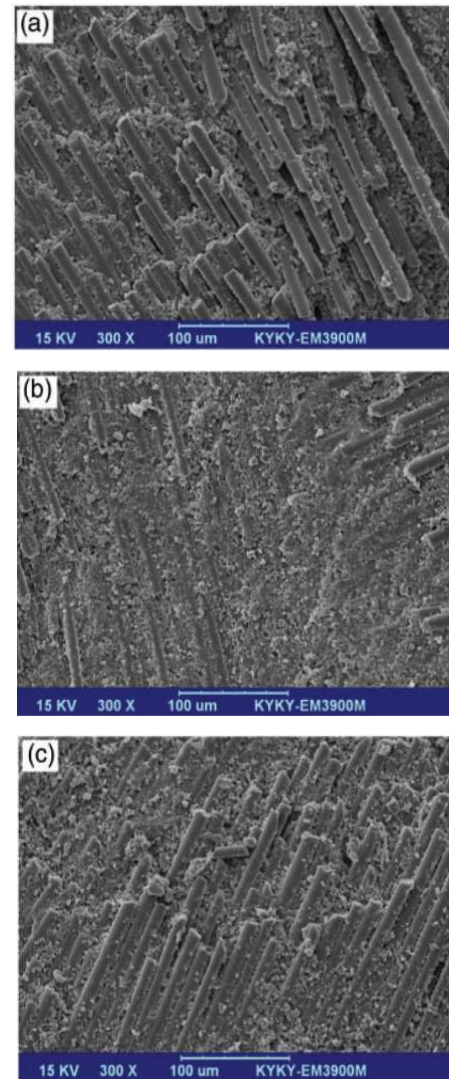


Fig. 17: SEM images of the worn surface (a), (b) and (c) neat basalt fiber-epoxy laminate, multiscale 0.1wt.% graphene oxide plus 1wt.% nanozirconia-enhanced sample and multiscale 0.5wt.% graphene oxide plus 3wt.% nanozirconia- enhanced sample, respectively. [18].

Joshua J Jensen et al. [7] mentioned in their study the value equal 0.25wt.% is an optimum doping content of the MWCNT doping to reach maximum damage response of carbon fiber CFRP laminate. Also, at this the optimum doping content value observed increasing in the energy absorption up to 18.03% in addition to 23.65% reduction in the rectangular damage area as compared to neat CFRP composite laminates (Fig. 18).

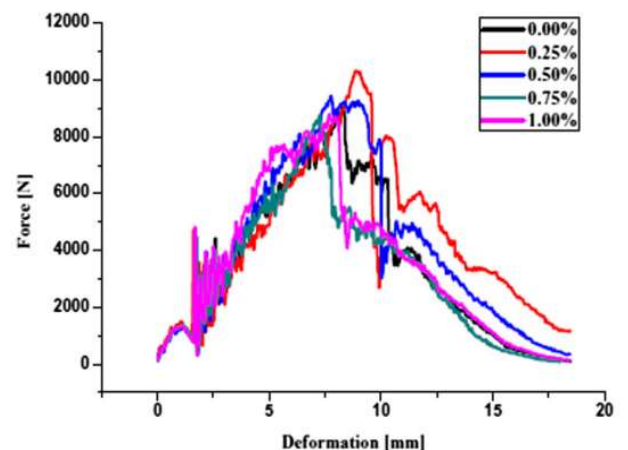


Fig. 18: Graph of force vs. deformation for different laminates [7].

This time by modification of fibers, Prasad Vishnu et al. [23] performed experimental study to evaluate flexural, tensile water absorption and interlaminar shear strength of unmodified and flax fiber composites coated by nano TiO_2 . They observed that in the results of this study an improvement in mechanical behavior on terms of tensile, interlaminar shear strength and flexural values by 22%, 16% and 24%, respectively. Also, reducing in water diffusion coefficient up to 42% on case of fiber coated specimens with 0.6wt.% nano TiO_2 , because this optimum percentage represents continuously and uniformly distribution of SiO_2 nanoparticles Fig. 19(a) and (b). However, towards a higher percentage of nanoparticles coating as in the case for 0.8wt.% TiO_2 , agglomeration and nonuniform distribution of particles over the fibers is witness (Fig. 19.c-d),(Fig. 19. e-f), (Fig. 19. g- h), (Fig. 19. i- j).

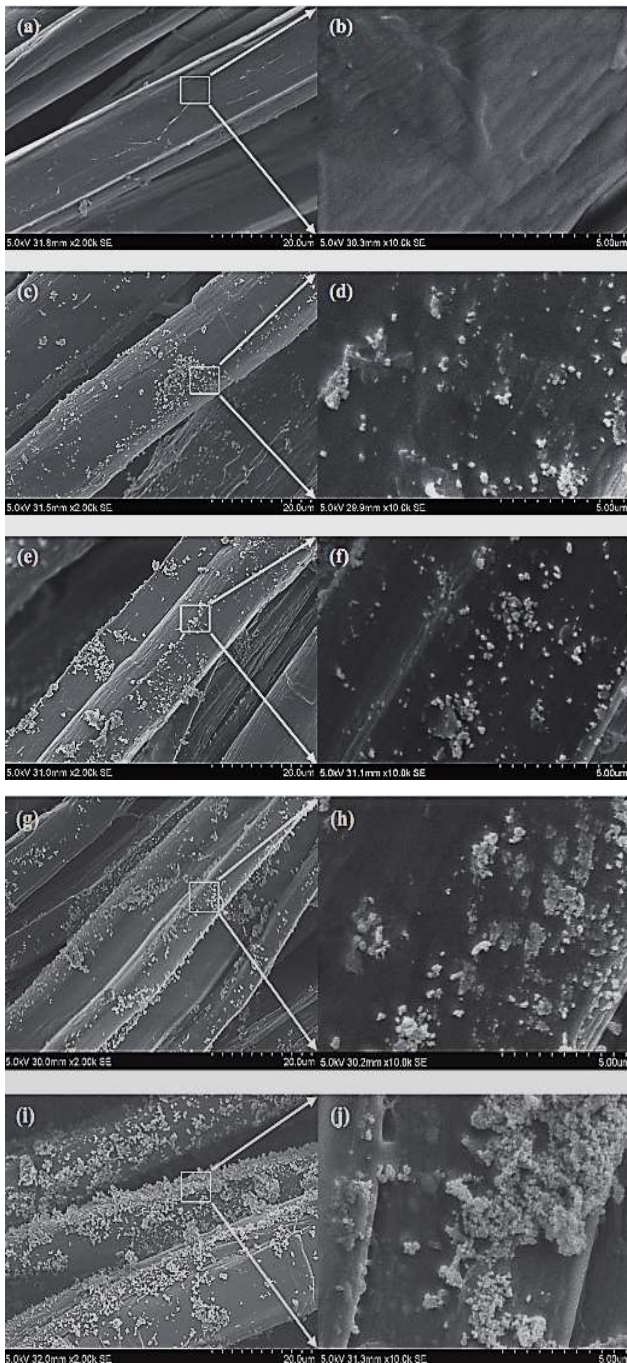


Fig. 19: SEM images of Flax fibers surface coated with TiO_2 at different content percentages (a) and (b) 0wt.%, (c) and (d) 0.2wt.%, (e) and (f) 0.4wt.%, (g) and (h) 0.6wt.%, (i) and (j) 0.8wt.%, [23].

A comparison between two nano particle (Al_2O_3 and SiO_2) with different volume fraction (0 to 2%), their effect on fatigue behavior of composites used for manufacture the prosthetic sockets carried out by Al Waily Muhannad et al. [37]. From the results of this study the authors noted that the mechanical behavior, fatigue response and strength property increase with composites reinforcement with nanoparticle. Also, the results showed that the modified with nano SiO_2 is better for fatigue limits than modified with other reinforcement nanoparticle for fatigue limits and the modified for fatigue strength lead to 60% more than fatigue limit without nanoparticle additive. For enhancing natural fiber-reinforced biocomposite behavior by addition zinc-oxide (ZnO) and compared with glass-fiber sheet molding compound (GF-SMC) in term of mechanical properties an experimental study was carried out by Wu Yingji et al. [28]. A newly developed biocomposite ($\text{ZnO}12.4\%$ -NFRBC) showed that increasing in flexural behavior, tensile strengths and water resistance by (121%), (38%) and (76%), respectively. when addition 12.4% ZnO nanoparticle, led to the this novel biocomposite for automotive application comparable on term of mechanical behavior as GF-SMC while the production consumed 9.2% less energy and reduced the environmental burden up to 33.2% from life cycle assessment. Also, led to high potential of the newly developed (NFRBC) to replace (GF-SMC) on automotive application. The use of the ZnO nanoparticle in the composites was also reported, it was emphasized that the ZnO particles were easily adsorbed from the fiber surface, which indicated good surface compatibility fiber/ ZnO particles (Fig. 20). Same phenomena was observed by authors on the case of other inorganic particle such as aluminum hydroxide ($\text{Al}(\text{OH})_3$) and magnetite (Fe_3O_4) which adhered on the surface of natural fibers.

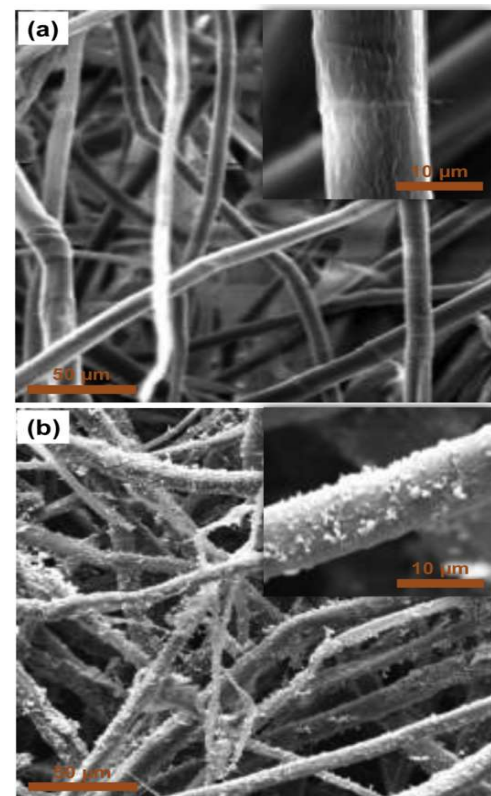


Fig. 20: Surface of Alkali-treated Kenaf fibers (a) before and (b) after loading by 17.8% ZnO nanoparticle, SEM images [28].

Parimala R et al. [20] were performed experimental study contained to evaluate of the mechanical behavior from tensile (Table 3) , flexural (Table 4) and impact test of carbon braided biaxial fibre composite material. The composite were fabricated by adding 0 wt.% to 5wt.% nanoparticles of TiO₂.

Table. III

TENSILE TEST VALUES OF BIAXIAL BRAIDED CARBON COMPOSITES WITH DIFFERENT PERCENTAGE OF TiO₂ NANOPARTICLE [20]

Specimen	Max load (KN)	Ultimate tensile strength (MPa)	Elongation break (%)	Tensile strength break (MPa)	Modulus (MPa)
0wt.%	12.03	130.16	24.04	103.67	1224.46
1wt.%	20.70	245.00	27.09	179.01	1658.23
3wt.%	23.66	267.51	29.05	192.55	1884.95
5wt.%	21.56	257.15	28.03	187.66	1724.69

Table. IV

FLEXURAL TEST VALUES OF BIAXIAL BRAIDED CARBON COMPOSITES WITH DIFFERENT PERCENTAGE OF TiO₂ NANOPARTICLE [20]

Specimen	Flexural load (N)	Max flexural stress (MPa)	Modulus (MPa)
0wt.% TiO ₂	229.36	165.79	8265.88
1wt.% TiO ₂	310.14	217.83	9515.62
3wt.% TiO ₂	329.29	254.82	14277.20
5wt.% TiO ₂	327.71	245.38	14181.26

After effectively adjusted carried out by researchers of this study with adding nanoparticle of TiO₂ in various percentage, the results show that the 3wt.% of the nanoparticle TiO₂ is the better percentage compared to other three configuration on mechanical behavior in term of flexural and tensile strength. And found that the flexural and tensile properties to decrease in the 5wt.% of TiO₂. In addition, the results show that no breakage up to 61dJ for all the samples in impact tests.

Size effect comparison of silica particle (nano and micro) on impact response of Carbon/Epoxy composite carried out by Dos Santos Julio C et al. [38]. The authors performed an incorporation of 1 and 3.5wt.% of both micro and nano-silica particles in plain weave carbon fiber/epoxy composite to evaluate the behavior of materials under impact tests. The authors were concluded that the micro size revealed better impact resistance compared to the nano particle size, when inclusion of 1wt.% of silica Vs. decreased in impact absorption when nano particle addition. This due to the interfacial fiber/matrix was increased by the silica nano sized and which might contribute to the fiber matrix bending weakening. The addition results also showed that the increase in mechanical behavior from tensile strength and modulus in adding nanosilica particle due to attributed to the interlocking of polymeric chains. A natural additive material was used in the study of Selvaraj DK et al. [22]. Powder from tamarind seeds TSP with 5% of the weight of the matrix incorporated in the composite to produce the laminate and compared between another laminate without additive on mechanical behavior (tensile, bending and moisture absorption tests). The main object of this investigation to develop a new natural fiber reinforced polymer composites NFRP and the influence of a natural additive in the composite. An essential conclude of this study is that the specimens with natural additive has a Young's modulus with increases up to 10% and ultimate tensile strength up to 6% compared to the composite without additive. And due to presence of natural additive material on the surface of the composite, it becomes more absorber than the specimens without additive. All these results indicate that the influence of TSP additive in enhancing the mechanical behavior of composite material is stronger with great scale.

Roy Samit et al. [39] performed compression test of pultruded composites to evaluate and determinate the compressive strength of these generally weak in compression. The authors prepared pultruded composites with nanoclay incorporation for different content (0, 1, 2, 3, 4, 5wt.% and 10wt.%). The compression tests of this material show that increase on compressive properties with increasing clay loadings up to 10wt.%, due to good interaction between the glass fibers silicon based and the silicate clays, indicate of enhanced adhered between matrix and fiber. Najafi Abdollah et al. [16] were investigated in the role of coupling agent (malcated polypropylene MAPP) presence. This study based in incorporation of nanoclay and MAPP with concentration 0, 2 and 4 per hundred compounds (phc) and 0 and 2phc, respectively. The results indicated that the impact response and water uptake of PP/reed flour nanocomposites decreased by addition of nanoclay. However, with nanoclay loading the tensile modulus property and strength of the composites increased. Knowing that these both mechanical and physical analyses properties showed that the biggest enhancement value for the nanoclay loading at 4phc. With proof of that by using the X-ray diffraction analyze, when observed better dispersion of nanoclay on composites and the highlight the role of MAPP coupling agent. Same observation in the work of Njuguna James et al. [44] when proved the role of the coupling agent on enhancing of the behavior such as mechanical properties of the nanocomposites. Faruk Omar and Matuana Laurent M [24] investigated at identifying the best system of incorporation the nanoparticles into composites. The first system involved a direct incorporation of nanoclay particle into material during conventional dry compounding which named (direct dry blending process). The second system consisted of the reinforcement of matrix with nanoparticle, which was then used the melt blending process. It finally, the melt blending process appeared to be the best system of incorporation of nanoparticle in the composites. Table 5 highlights one of the results of mechanical analysis study show the influence of blending process of nanoparticle.

Table. V

FLEXURAL PROPERTIES OF NANOCOMPOSITE ON TWO DIFFERENT PROCESSES OF BLENDING [24]

Blending process	Flexural behavior	
	Strength (MPa) ^a	Modulus (MPa) ^a
Control (no nanoclay)	28.9±1.4 ^A	1919.7±112 ^A
Direct dry blending (direct mix)	27.1±1.4 ^B	2233.8±144 ^B
Melt blending	33.5±0.4 ^C	2726.9±196 ^C

V. CONCLUSION AND FUTURE DIRECTION

In summary, particle materials have been used as precious parts to improve the properties of different existing materials. From this review we concluded that:

- The additive can be added only in minimal percentage to enhance behavior of composites.
- The size, type and hybridization of particles addition are some of the parameters to predict and analyze of behavior and damage modes of the material.
- We found that the use of additive according to tests applications.
- A few recherches studies in case of behavior of sandwich composites with particles addition.
- The use of natural additive type will be potential filler material for composite materials and it is sustainable by nature.

Although significant previous works is done in this area, further work should be conducted for advancement of this research field such as:

- The use of NDT carrying out to ensure zero defect in composites to give good estimation of materials strength.
- Find more investigations to subject the use of coated fibers in the composite materials in the cryogenic conditions for special application such as aerospace applications, because the majority of research on the coated fibers was concentrated studies at the high and ambient temperature environment.
- The search in the behavior of composite materials reinforced by the particle addition in matrix and coated fibers on the same time.
- Conducting in-depth research on incorporation process of the particles.
- Performed numerical investigations to predict the effect of the particles addition on mechanical, thermal and physical properties of materials for different applications.

ACKNOWLEDGMENT

The author would like to thank the Ministry of Higher Education and Scientific Research, Algeria. Also gratefully acknowledges the Algerian General Direction of Research and Development Technology (DGRSDT) for their supports. And thanks to the Direction of Research Center in Industrial Technology-CRTI, Algeria for supporting this study. The author like to thanks to the family and to thanks to the members team of Nondestructive Testing and evaluation by Ultrasound for their patience with him on crossing the path of knowledge.

REFERENCES

- [1] Lee, B.-H., H.-J. Kim, and W.-R. Yu, Fabrication of long and discontinuous natural fiber reinforced polypropylene biocomposites and their mechanical properties. *Fibers and Polymers*, 2009. 10(1): p. 83-90.
- [2] Sharma, G., et al., Novel development of nanoparticles to bimetallic nanoparticles and their composites: a review. *Journal of King Saud University-Science*, 2019. 31(2): p. 257-269.
- [3] Hári, J. and B. Pukánszky, Nanocomposites: preparation, structure, and properties, in *Applied plastics engineering handbook* 2011, Elsevier. p. 109-142.
- [4] Mohajerani, A., et al., Nanoparticles in construction materials and other applications, and implications of nanoparticle use. *Materials*, 2019. 12(19): p. 3052.
- [5] Venkatesh, N., H. Bhowmik, and A. Kuila, Metallic nanoparticle: a review. *Biomedical Journal of Scientific & Technical Research*, 2018. 4(2): p. 3765-3775.
- [6] Ferrando, R., J. Jellinek, and R.L. Johnston, Nanoalloys: from theory to applications of alloy clusters and nanoparticles. *Chemical reviews*, 2008. 108(3): p. 845-910.
- [7] Joshua, J.J., P. Venkatanarayanan, and D. Singh, A literature review on composite materials filled with and without nanoparticles subjected to high/low velocity impact loads. *Materials Today: Proceedings*, 2020. 33(7): p. 4635-4641.
- [8] Saba, N., P.M. Tahir, and M. Jawaaid, A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. *Polymers*, 2014. 6(8): p. 2247-2273.
- [9] Kumar, A., et al., Polyacrylamide/NiO. 02ZnO. 98O nanocomposite with high solar light photocatalytic activity and efficient adsorption capacity for toxic dye removal. *Industrial & Engineering Chemistry Research*, 2014. 53(40): p. 15549-15560.
- [10] LeBaron, P.C., Z. Wang, and T.J. Pinnavaia, Polymer-layered silicate nanocomposites: an overview. *Applied clay science*, 1999. 15(1-2): p. 11-29.
- [11] Landowski, M., et al., Impact damage in SiO₂ nanoparticle enhanced epoxy–Carbon fibre composites. *Composites Part B: Engineering*, 2017. 113: p. 91-99.
- [12] Di, C., et al., Study of hybrid nanoparticles modified epoxy resin used in filament winding composite. *Materials*, 2019. 12(23): p. 3853.
- [13] Vashisth, A., et al. Effects of Nanosilica on the Ballistic Impact Tolerance of Carbon/Epoxy Tubes Loaded in Torsion. in *Annual Forum Proceedings-AHS International*. 2017. American Helicopter Society.
- [14] Tsai, S.-N., et al., Fracture and fatigue behaviour of carbon fibre composites with nanoparticle-sized fibres. *composite structures*, 2019. 217: p. 143-149.
- [15] Ebrahimnezhad-Khaljiri, H., R. Eslami-Farsani, and S. Talebi, Investigating the High Velocity Impact Behavior of the Laminated Composites of Aluminum/Jute Fibers-Epoxy Containing Nanoclay Particles. *Fibers and Polymers*, 2020. 21(11): p. 2607-2613.
- [16] Najafi, A., et al., The impact of the nature of nanoclay on physical and mechanical properties of polypropylene/reed flour nanocomposites. *Journal of Thermoplastic Composite Materials*, 2012. 25(6): p. 717-727.
- [17] Tuncer, C. and O. Canyurt, The effect of nanoparticle additive on the mechanical properties of glass fiber composite materials. *ACTA PHYSICA POLONICA A* 2019. 135(4): p. 752-755.
- [18] Toorchi, D., E. Tohidlou, and H. Khosravi, Enhanced flexural and tribological properties of basalt fiber-epoxy composite using nano-zirconia/graphene oxide hybrid system. *Journal of Industrial Textiles*, 2020: p. 1528083720920573.
- [19] Dolez, P.I., et al., Hydrophobic treatments for natural fibers based on metal oxide nanoparticles and fatty acids. *Procedia engineering*, 2017. 200: p. 81-88.
- [20] Parimala, R. and D. Jabaraj, Carbon braided biaxial fiber composite with TiO₂: Mechanical properties. in *2014 International Conference on Science Engineering and Management Research (ICSEMR)*. 2014. IEEE.
- [21] Reis, P., et al., Viscoelastic behaviour of composites with epoxy matrix filled by cork powder. *composite structures*, 2020. 234: p. 111669.
- [22] Selvaraj, D., et al., Influence of the natural additive on natural fiber reinforced thermoplastic composite. *Procedia Manufacturing*, 2019. 38: p. 1121-1129.
- [23] Prasad, V., K. Sekar, and M. Joseph, Mechanical and water absorption properties of nano TiO₂ coated flax fibre epoxy composites. *Construction and Building Materials*, 2021. 284: p. 122803.
- [24] Faruk, O. and L.M. Matuana, Nanoclay reinforced HDPE as a matrix for wood-plastic composites. *Composites Science and Technology*, 2008. 68(9): p. 2073-2077.
- [25] Shalwan, A. and B. Yousif, Influence of date palm fibre and graphite filler on mechanical and wear characteristics of epoxy composites. *Materials & Design*, 2014. 59: p. 264-273.
- [26] Hanemann, T. and D.V. Szabó, Polymer-nanoparticle composites: from synthesis to modern applications. *Materials*, 2010. 3(6): p. 3468-3517.
- [27] Olar, R., Nanomaterials and nanotechnologies for civil engineering. *Buletinul Institutului Politehnic din Iasi. Sectia Constructii, Arhitectura*, 2011. 57(4): p. 109.
- [28] Wu, Y., et al., Development and evaluation of zinc oxide-blended kenaf fiber biocomposite for automotive applications. *Materials Today Communications*, 2020. 24: p. 101008.
- [29] Presting, H. and U. Konig, Future nanotechnology developments for automotive applications. *Mater. Sci. Eng. C* 2003. 23: p. 737-741.
- [30] Kamel, S., Nanotechnology and its applications in lignocellulosic composites, a mini review. *eXPRESS Polym. Lett*, 2007. 1: p. 546-575.
- [31] Abu-Okail, M., et al., Effect of dispersion of alumina nanoparticles and graphene nanoplatelets on microstructural and mechanical characteristics of hybrid carbon/glass fibers reinforced polymer composite. *journal of materials research and technology*, 2021. 14: p. 2624-2637.
- [32] Shubha, P., et al., Ex-situ fabrication of ZnO nanoparticles coated silk fiber for surgical applications. *Materials Chemistry and Physics*, 2019. 231: p. 21-26.
- [33] L., Y., Property improvement of polyarylacetylene matrix composites by phenolic resins. *Fibre Reinf. Plast./Compos*, 2001. 3: p. 22-4.
- [34] HJ, F., H. YD, and L. L., Influence of fibre surface oxidation treatment on mechanical interfacial properties of carbon fibre/ polyarylacetylene composites. *Mater Sci Technol* 2004. 20: p. 1655-60.
- [35] Memduh Kara, et al., Impact behavior of carbon fiber/epoxy composite tubes reinforced with multi-walled carbon nanotubes at cryogenic environment. *Composites Part B*, 2018. 145: p. 145-154.
- [36] Koricho, E.G., et al., Effect of hybrid (micro-and nano-) fillers on impact response of GFRP composite. *composite structures*, 2015. 134: p. 789-798.

- [37] Al-Waily, M., M.H. Tolephih, and M.J. Jweeg. Fatigue Characterization for Composite Materials used in Artificial Socket Prostheses with the Adding of Nanoparticles. in IOP Conference Series: Materials Science and Engineering. 2020. IOP Publishing.
- [38] Dos Santos, J.C., et al., Impact Behaviour Of Hybrid Carbon Fibre Reinforced Composites With Micro And Functionalized Nano Silica Particles. Bccm-3 – Brazilian Conference on Composite Materials, 2016.
- [39] Roy, S., et al. Compressive strength enhancement of pultruded thermoplastic composites using nanoclay reinforcement. in 45th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics & Materials Conference. 2004.
- [40] Chandradass, J., M.R. Kumar, and R. Velmurugan, Effect of nanoclay addition on vibration properties of glass fibre reinforced vinyl ester composites. *Materials Letters*, 2007. 61(22): p. 4385-4388.
- [41] Kord, B., Nanofiller reinforcement effects on the thermal, dynamic mechanical, and morphological behavior of HDPE/rice husk flour composites. *BioResources*, 2011. 6(2): p. 1351-1358.
- [42] Fu, S.-Y., et al., Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites. *Composites Part B: Engineering*, 2008. 39(6): p. 933-961.
- [43] Arulvel, S., et al., A comprehensive review on mechanical and surface characteristics of composites reinforced with coated fibres. *Surfaces and Interfaces*, 2021. 27: p. 101449.
- [44] Njuguna, J., et al., Natural fibre-reinforced polymer composites and nanocomposites for automotive applications, in *Cellulose fibers: bio- and nano-polymer composites* 2011, Springer. p. 661-700.



Fares Mohammed Laid REKBI was born in Touggourt, Algeria, in 1986. In 2010 received the degree of Master in mechanical engineering, from Mohamed Khider Biskra University. In 2016 he obtained the Ph.D. in mechanical engineering from Mohamed Khider Biskra University, Algeria. He is currently a professor researcher class A at research

center in industrial technologies CRTI, Algiers, Algeria. His main research areas are in composite materials, non-destructives testing, bio-composite materials.

Electrochemical Measurements of Ni / Graphene based Nanohybrids for Electrochemical Energy Storage “Supercapacitors”

Ikram Djebablia, Ouanassa Guellati, Naima Habib, Aicha Harat, Fahima Djefaflia, Aissa Nait-Merzoug,

Izabela Janowska and Mohamed Guerioune

Abstract– Given the issues related to the use of fossil fuels and water pollution, the development and the application of new smart nanomaterials for supercapacitors and biosensors has become a vital issue for human and industrial societies. Therefore, nanotechnology has given more interest to these areas via micro/nanosystems or nanohybrids characterized by interesting composition, significant porosity and texture at nanoscale. In this work, we have produced electroactive nanohybrids based on in-situ Ni mono-hydroxide few layers Graphene oxide "GO" using a simple and low cost hydrothermal technique under well-studied thermodynamic conditions (120 and 180 °C growth temperature), for performant supercapacitor devices. We have carried out the structural, morphological, textural and optical characterization of these products and consequently we have specified the relationship between their physico-chemical characteristics and their electrochemical properties for ulterior application. Thus, we have carried out various electrochemical measurements through Cyclic Voltammetry tests and we have marked the important electrochemical properties of these Ni/Graphene nanohybrids in two NaOH electrolyte concentrations (0.1 and 1 M) in order to improve the performance of supercapacitors, which have become a socio-economic issue with this nanotechnological development. Consequently, these obtained Ni/Graphene nanohybrids have shown a very interesting electrochemical results with specific capacities 1863 and 253 F.g⁻¹ for the case of nanohybrid obtained at 6h/120°C in NaOH aqueous electrolyte with two different concentrations (1 and 0.1M), respectively. However, for a fixed electrolyte concentration of 1M NaOH, both nanohybrids obtained at 120 and 180°C gave specific capacity values around 1863 and 2981 F.g⁻¹, respectively.

Keywords– Energy storage, Supercapacitors, Nanohybrid, Ni Hydroxide, Graphene Oxide, Electrochemical measurement.

I. INTRODUCTION

The rapid development of human society has led to an ever-growing demand for energy and serious problems like global warming and environmental pollution [1, 2]. At the same time, the dependence of modern societies on fossil fuels and the rapid strides made in various areas such as industrialization has contributed also to these growing energy requirements. Reducing these issues is an increasingly important goal that can be achieved through developing other low-cost, clean and sustainable energy sources/storage technologies. Thus,

renewable sources (RSs) such as solar, hydro and wind energy have become widely endorsed solutions for addressing these concerns [3].

However, due to the large fluctuations in their generation, produced electricity from these renewable energy sources must be efficiently stored to supply the world with energy on demand. Energy storage systems (ESSs) are the key to deal with the intermittent nature of renewable energy sources and increase the power transmitted into the grid from systems such as wind and solar power. In this context, considerable efforts have been put into researching and developing most effective and practical technologies for more efficient electrochemical energy storage devices like: batteries, fuel cells and supercapacitors (SCs) [4, 5].

In recent years, SCs also referred to electrochemical capacitor or ultracapacitor [5, 6] have attracted significant attention, mainly due to their high power density, long life cycle and higher charging/discharging rate capability [7]. While the energy density of supercapacitors is very high compared to conventional dielectric capacitors but it is still significantly lower than batteries, which limits their adoption to those applications that require high life cycle and power density [8]. Coupling with batteries (or another power source) is still required for supplying energy to longer periods of use. Thus, there is a strong interest for increasing this supercapacitors energy density to be closer to those of batteries.

In order to overcome this low energy density obstacle, different nanomaterials including carbonaceous nanomaterials [6], mixed metal oxides/hydroxides [9, 10] and

Manuscript received October 9, 2022; revised April 22, 2023.

I. Djebablia is with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA. (e-mail: ikramdjebablia@gmail.com)

N. Habib, F. Djefaflia, A. Nait-Merzoug and O. Guellati are with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA and LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: habib.naima23@yahoo.fr, djefafliafahima@gmail.com, abenlala@yahoo.fr, guellati23@yahoo.fr)

A. Harat and M. Guerioune are with LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: harat_aicha@yahoo.fr and mguerioune@yahoo.fr)

I. Janowska is with ICPEES Institute, ECPM - CNRS, UdS, 25 Rue Becquerel, 67087 Strasbourg, FRANCE. (email: janowskai@unistra.fr)

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.158

conducting polymers [11-13] have been used as supercapacitor electroactive functional materials. Carbon, in its various forms like Single (SWNTs) and Multi (MWNTs) Walled Carbon NanoTubes [14], activated carbon fibers (ACFs) [15, 16] and carbide derived carbons (CDCs) [17], owing to a unique properties combination, such as: high surface area, lightweight, good electrical conductivity and high temperature stability [6]. However, the application of these individual carbonaceous nanomaterials in supercapacitors is limited by their high cost and unsatisfactory electrochemical performance [18]. Due to their superior electrical conductivity, high theoretical surface area of over $2600 \text{ m}^2 \cdot \text{g}^{-1}$, optical and mechanical important properties [19, 20], Graphene as monolayer of graphite is expected to play a crucial role for energy applications in many fields especially in elastic and flexible electronic devices [21] as well as photovoltaics [22]. Recently, it has been proposed that this kind of nanomaterial should be a competitive electroactive material for supercapacitors application [23]. Unfortunately, due to the unavoidable aggregation of Graphene films, their surface area is usually much lower than the theoretical value and its capacitance is generally in the range [100–200 F] [24, 25]. In addition, they suggest the Graphene oxide which is a single sheet of Graphite oxide but it possesses less p-p stacking stability, poor conductivity and thus it has been theoretically claimed that it is not able to directly serve as the electrode material for supercapacitors [26]. Thereby, numerous studies have been focused on investigating earth-abundant alternatives transition metal oxides (Mn, Ni, Fe and Co) [27, 28] and transition metal layered double hydroxides (LDH) [29] as pseudo-capacitance storage materials. Among these alternatives, Ni compounds have captured in recent years tremendous research attention due to their high speed reversible surface redox reactions [30]. In particular, $\text{Ni}(\text{OH})_2$ possesses a specific properties like high power density, excellent cyclability, high specific energy and low toxicity [31]. Nevertheless, their relatively low conductivity and limited surface area restricts their further application.

Furthermore, carbon with metal oxides or hydroxides based nanocomposites/nanohybrids have attracted great interest with high capacitances and good cycling performances [32, 33]. Recently, nanocomposites based on $\text{Ni}(\text{OH})_2$ and carbon materials have been prepared and used as supercapacitors electrode. For instance, $\text{Ni}(\text{OH})_2$ / 3D Graphene nanohybrid were prepared by C. Jiang's group via atmospheric pressure chemical vapor deposition (APCVD) and shows high specific capacitance around $1450 \text{ F} \cdot \text{g}^{-1}$ at a current density of $5 \text{ A} \cdot \text{g}^{-1}$ [34]. H. Wang et al. obtained 3D $\text{Ni}(\text{OH})_2$ /GO hybrid through a two-step process and their specific capacitance have shown 90% retention after 10000 charge/discharge cycles [35]. Additionally, J. Liu et al. have synthesized using a brief and facile hydrothermal method a 3D rose-like $\text{Ni}(\text{OH})_2$ /rGO nanohybrid with specific capacity around $802 \text{ F} \cdot \text{g}^{-1}$ at $2 \text{ A} \cdot \text{g}^{-1}$ [36].

Consequently in this paper, we present the successful synthesis of $\text{Ni}(\text{HCO}_3)_2$, $\alpha\text{-3Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ and their nanohybrids with Graphene oxide using a facile and low cost urea based free template hydrothermal method at different optimized conditions. The new kind of Ni hydroxide based nanohybrids which are different than those obtained in literature have shown very interesting structural, optical and electrochemical properties for performant supercapacitor devices. Their electrochemical measurements through Cyclic Voltammetry (CV) tests in two different NaOH electrolyte concentrations (0.1 and 1 M) show a very interesting specific capacities of 253 and $1863 \text{ F} \cdot \text{g}^{-1}$, respectively, for the case of nanohybrid obtained at 6h/120°C. However, for a fixed 1M

NaOH electrolyte concentration, both nanohybrids obtained at 120 and 180°C hydrothermal growth temperature process gave specific capacity values around 1863 and $2981 \text{ F} \cdot \text{g}^{-1}$, respectively.

II. EXPERIMENTAL PROCEDURE

All the chemicals, urea (Merck, purity $\geq 98\%$), Ni chloride (Sigma-Aldrich, purity $\geq 99,99\%$), were of analytical grade and were used without further purification. Ni Foam (NiF) was purchased from (Alantum, Munich, Germany) with areal density of $420 \text{ g} \cdot \text{m}^{-2}$ as well as a diameter and a thickness of 16 mm and 0.2 mm, respectively.

A. *Ni and Ni/Graphene nanohybrids synthesis*

0.1M Ni (II) chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) with and without Graphene was dissolved in deionized water for 5 min at room temperature. After that, 0.5 M urea ($\text{CH}_4\text{N}_2\text{O}$), which is highly soluble in water, was added into the solution and ultrasonicated for 15 min until a green transparent or black green solution was obtained. The last dispersed solution was transferred into a 40 mL Teflon-lined hydrothermal autoclave system. The autoclave was sealed, maintained at two different growth temperatures (120 and 180°C) during 6 hours and then allowed to cool down naturally to room temperature. The obtained products with distinct colors were filtered and washed several times with distilled water and ethanol before drying in an oven at 80°C overnight.

B. *Working electrode preparation*

The working electrodes for electrochemical performance evaluation of Ni/Graphene nanohybrid material were prepared as follows: firstly, a mixture containing 80 wt.% of Ni or Ni/GO based electroactive materials, 10 wt.% of carbon black (CB) and 10 wt.% of PVdF binder with some drop of NMP solvent was well mixed in an agate mortar to form a paste. This was spread onto a $1 \times 1 \text{ cm}^2$ area of pre-treated NiF and dried at 80°C in an oven for 24 h to ensure complete evaporation of the NMP.

C. *Characterization techniques*

Detailed physico-chemical properties of these samples were examined by using various analysis tools :

The structural characterization of these nanohybrid products were investigated using powder X-ray diffraction (XRD) via an XRD D8 ADVANCE-BRUKER AXS diffractometer equipped with a copper anticathode tube "Cu K α radiation" ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA with a scanning rate of $0.2^\circ \cdot \text{s}^{-1}$. In addition, their Fourier-Transform Infra-red (FTIR) spectra were recorded using a Bruker Vertex 77v spectrometer in the wave number range [from 400 to 4000 cm^{-1}] with 4 cm^{-1} resolution and analyzed with an Opus software.

Moreover, the thermal stability of these products were measured using a Thermo Gravimetric Analysis technique, which was carried out using TA Instruments Q5000 Simultaneous (DSC/TG) analyzer which allows the measurements of the weight change in the products as a function of temperature under air atmosphere from 30°C to 1000°C with $10^\circ\text{C}/\text{min}$ heating rate.

However, the products morphology were analyzed using a Field Emission Scanning Electron Microscopy (JEOL 6700-FEG microscope) operating at 3 kV.

The absorbance spectra of the samples were obtained using UV-Vis spectrophotometer to investigate the optical properties of these nanoparticles. The spectral absorption were recorded using ThermoScientific™ GENESYS 10S UV-Visible spectrometer in the wave length range [100 to 1100 nm] using quartz cuvettes at room temperature.

The electrochemical measurements were carried out using a Gamry R600 potentiostat (USA) under ambient temperature in a three-electrode cell setup using NaOH aqueous electrolyte (with two different molarities 0.1 and 1 M) with Pt (platinum) and Hg/HgO (mercuric oxide) counter and reference electrode, respectively.

III. RESULTS AND DISCUSSION

The purity and the crystallinity of as-synthesized products were examined by powder XRD diffraction. Figure 1 illustrates the synthesized Ni mono-hydroxide and their nanohybrid with Graphene using free template hydrothermal growth technique at optimized conditions.

For the case of 6h/120°C synthesis condition, four peaks are observed at 12.06°, 33.84°, 35.52° and 59.80° assigned to the (001), (110), (111) and (300) crystal planes, respectively; characterizing the hexagonal structure " α -3Ni(OH) $_2$ ·2H $_2$ O" formation according to JCPDS card number [00-022-0444] with P-31m symmetry and $a = 5.29352 \text{ \AA}$ / $c = 7.32841 \text{ \AA}$ estimated crystalline parameters which are similar to the reported values in the literature [37, 38]. Additionally, no impurity peaks can be found in these XRD patterns.

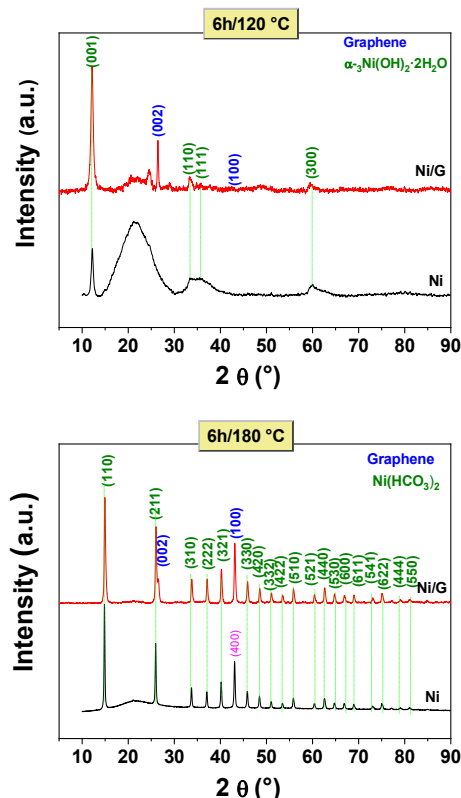


Fig. 1: XRD diffractograms of Ni mono-hydroxide and their Ni/Graphene nanohybrid synthesized by hydrothermal process at two different growth temperatures (120 and 180°C).

On the other hand, a second phase proving the existence of Graphene was found with its two characteristic peaks located at 26.45° and 43.02° corresponding, respectively, to the crystal planes (002) and (100) which in accord with the literature [39, 40]. However, in the second 6h/180°C synthesis condition, we notice a radical change on the formed structure

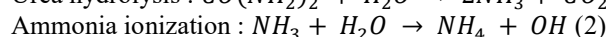
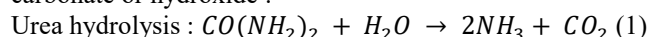
of these products due to the effect of growth temperature. So, we obtained a well crystallized phase with narrow peaks of Ni hydrogen carbonate " $\text{Ni}(\text{HCO}_3)_2$ " with a centered cubic structure according to JCPDS card number [00-015-0782] [41, 42]. This structure is recognized through its most intense peaks located at 14.80°, 26.1°, 33.70°, 37.02°, 40.34° corresponding to the crystalline planes (110), (211), (310), (222) and (321), respectively (Table I). Moreover, in the same way for their nanohybrids, we found Graphene with his two characteristic peaks at 26.54° (002) and 43.16° (100) [43]

Table. I
CALCULATED CRYSTALLINE PARAMETERS FOR Ni MONO-HYDROXIDE AND THEIR Ni/GRAPHENE NANOHYBRID.

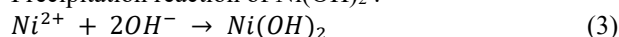
Phase/Ref	Crystalline parameters		
	a (Å)	b (Å)	c (Å)
α - 3Ni(OH) $_2$ ·2H $_2$ O 22-0444	5.29352	5.29352	7.32841
Ni(HCO $_3$) $_2$	8.45699	8.45699	8.45699
15-0782	8.38300	8.38300	8.38300

confirming thus the nanohybrid formation as in the previous growth condition.

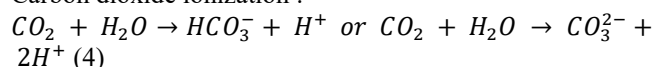
Consequently, we suggest the following main reactions of the urea homogeneous hydrolysis method for the synthesis of Ni carbonate or hydroxide :



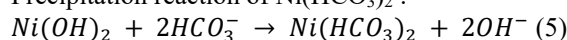
Precipitation reaction of Ni(OH) $_2$:



Carbon dioxide ionization :



Precipitation reaction of Ni(HCO $_3$) $_2$:



For further composition study of these products based of Ni mono-hydroxide and their (Ni/Graphene) nanohybrids, the FT-IR spectra of samples are investigated and shown in figure 2 (a & b). Common vibration bands are observed in the first case of 120°C at 3633 cm $^{-1}$, [2358-2363 cm $^{-1}$], 2231 cm $^{-1}$, 1363 cm $^{-1}$, 631 cm $^{-1}$ and 641 cm $^{-1}$. The narrow absorption located at around 3645 cm $^{-1}$ is ascribed to the -OH in the brucite-like structure [44]. The band around [2358-2363 cm $^{-1}$] corresponds to the bending mode of water molecules [44, 45]. The strong absorption band at 2231 cm $^{-1}$ indicates the presence of impurities C $\equiv$ N due to the used urea [46]. Two narrow peaks, which appear at 641 and 631 cm $^{-1}$ in the low wave number region, correspond to the bending of Ni-OH due to the elongation vibration of Ni(OH) $_2$ existing in this synthesized Ni mono-hydroxide with and without Graphene oxide [44-46]. Same peaks are observed also in the case of 180 °C, beyond a narrow peak at 3260 cm $^{-1}$ which is ascribed to rise from hydrogen-bonded OH stretching [4] and C=O elongation vibration peaks which are observed at 1553 and 2358 cm $^{-1}$ [44, 45]. Beside the existence of peaks in the range of [1365 – 1380 cm $^{-1}$] that are attributed to C-O vibration band of carbonate anions and Graphene network [39].

Furthermore, the thermal decomposition behavior investigation using TGA and DTG analyses is shown in figure 3. Four to three distinct regions of weight loss were observed in the TGA curves between 200-800°C, afterwards the sample remains stable, depending on the nanocomposite component phases.

The corresponding weight loss between [27-230 °C] at around 12 wt.% is attributed to the evaporation of inter-layered water molecules in Ni hydroxides (for 6h/120°C) [44]. Meanwhile, the corresponding weight loss between [230 – 500 °C] around 23 wt.% was derived from the transformation of hydroxide to their oxide [44]. Finally, the 7 wt.% weight loss found between [500 – 800 °C] is due to the oxidation of nanostructured basic carbon type graphene to CO₂.

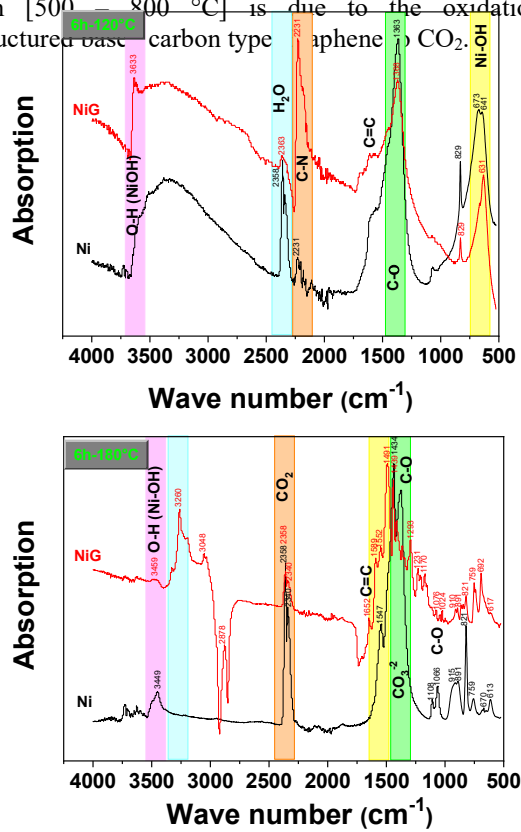


Fig. 2: FT-IR spectra of Ni mono-hydroxide and their Ni/Graphene based nanohybrid synthesized by hydrothermal process at two different conditions (6h/120°C and 6h/180°C).

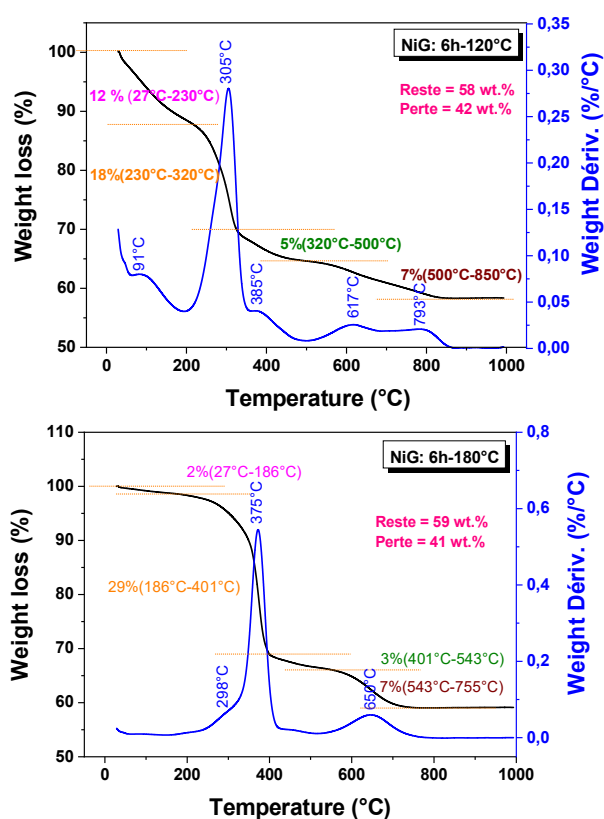


Fig. 3: TGA/DTA results of Ni hydroxide/Graphene based nanohybrid synthesized by hydrothermal process at two different conditions (6h/120°C and 6h/180°C).

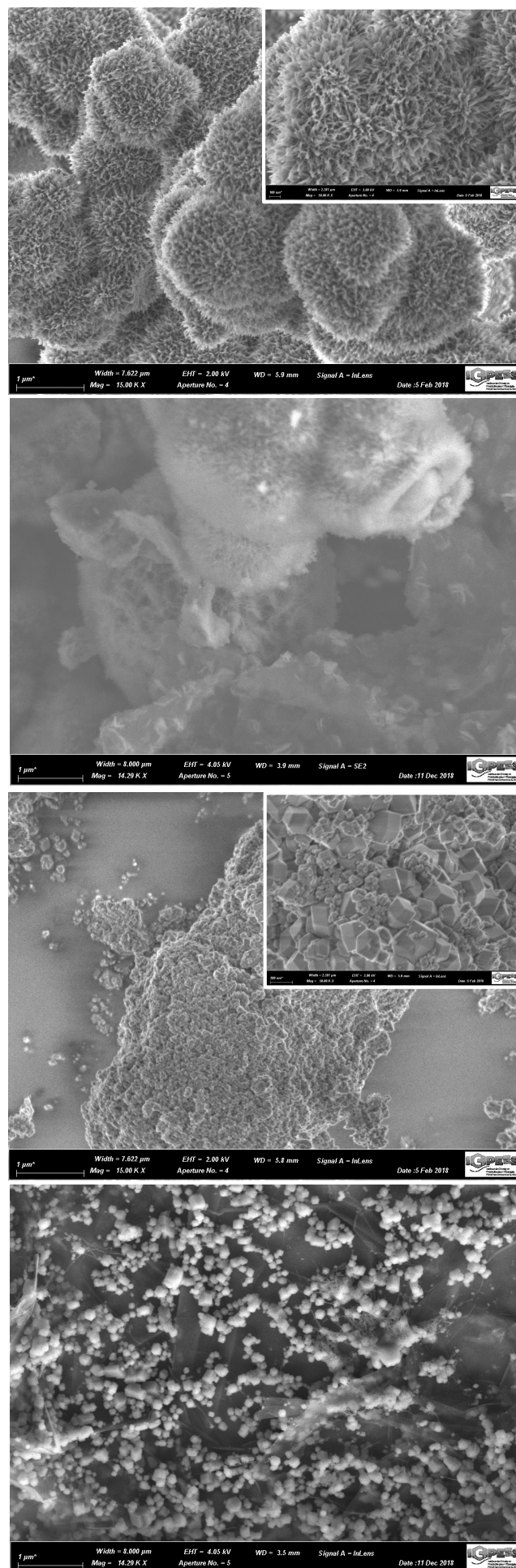


Fig. 4: FESEM micrographs of synthesized Ni based mono-hydroxide (a, c) and their nanohybrids (Ni hydroxide/Graphene) (b, d) : 6h/120°C (a, b) and 6h/180°C (c, d).

Similarly, for the nanohybrid synthesized at 6h/180°C, the mass losses are 2, 29, 3 and 7 wt.% at oxidation temperatures found in the ranges: [27-186 °C], [186-401 °C], [401-543 °C] and [543-755 °C] confirming also the existence of water evaporation due to the presence of -OH radicals, oxidation of carbonate to CO₂ and transformation of Ni hydroxide to oxide without forgetting the Graphene oxidation [44]. At the end, the overall mass loss of these nanohybrid products synthesized at 6h/120°C and 6h/180°C is around 42 and 41 wt.%, respectively. From these thermal results, we can estimate the nanohybrid composition to be metal/carbon = 90/10 wt.% which may have surely a benefic effect on the electrochemical behavior.

In order to follow the morphological and textural aspect of these produced nanomaterials, FESEM microscopy was carried out on these samples of Ni based mono-hydroxide and their nanohybrid (Ni/Graphene) hydrothermally synthesized at 120 and 180°C during 6 hours (Fig. 4). Firstly, we can clearly observe in the case of 6h/120°C (pure Ni mono-hydroxide), a formation of quasi micro-nanospheres at 3D with a porous texture and with well dispersed porosity due to an organized assembly of nano-needles (Fig. 4 a) [47]. These quasi micro-nanospheres with a porous texture have diameters around 2.5 µm. On the other hand, the micrograph represented in figure 4(b) confirms the formation of two nanostructures in the form of well dispersed last micro-nanospheres supported by Graphene nanosheets. However, for products of 6h/180°C (pure hydrogen carbonate Ni), we have obtained nanostructured particles (nanospheres, nanocubs, ...) (Fig. 4c) which are different than that of the previous condition product confirming thus the effect of growth temperature on the products morphology which affect therefore their ulterior properties. In addition, figure 4(d) shows these nanostructured particles supported by Graphene oxide sheets forming consequently the in-situ nanocomposites.

Optical Properties

Another spectroscopic analysis technique has been used in order to determine the optical properties that allow us to deduce the gap energies of these synthesized products [48]. The optical absorption spectra are shown in figure 5.

They show an absorption threshold at about 938-1010 nm in the case 6h/120°C which can be attributed to a transition of electrons from the valence to the conduction band. Further, in the case of 6h/180°C, a continuous absorption spectrum is observed from 200 to 1100 nm with a slight adsorption in the same range.

Table. II

ESTIMATED GAP ENERGY EG FOR NI MONO-HYDROXIDE AND THEIR GRAPHENE/NI NANOHYBRID

Products	Gap optique Eg (eV)			
	Direct		Indirect	
	120 °C	180 °C	120 °C	180 °C
α -Ni(OH) ₂	5.10	4.44	4.54	4.12
Graphene/ α -Ni(OH) ₂	4.90	3.50	4.35	3.21

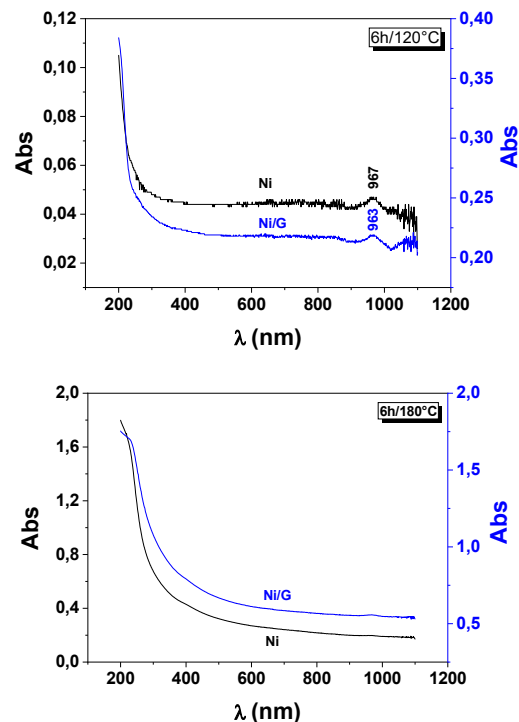


Fig. 5: Adsorption spectra of these products for two cases: 6h/120°C (a) and 6h/180°C (b).

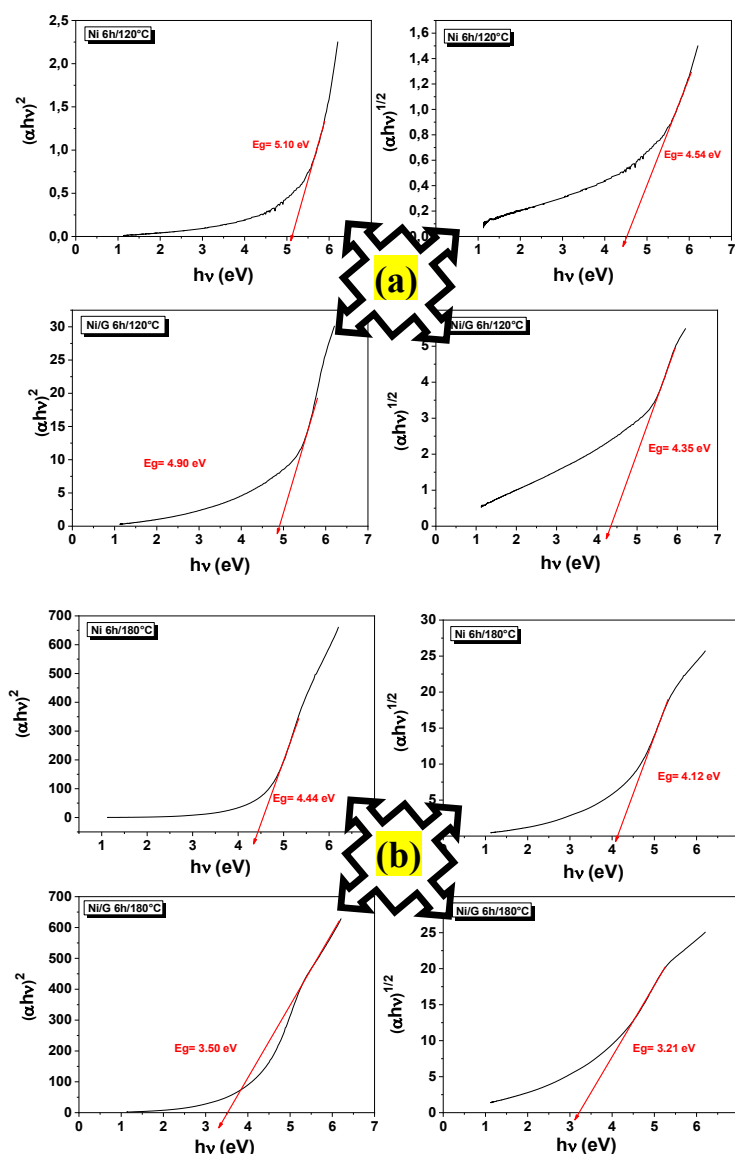


Fig. 6: Eg values for these synthesized products at two hydrothermal conditions: 6h/120°C (a) and 6h/180°C (b).

The gap band energy value (E_g) was calculated by using the following standard Tauc expression [45]: $(\alpha h\nu) = k(h\nu - E_g)$

where α is the absorption coefficient, k is a constant, $h\nu$ is the incident photon energy, E_g is the gap band energy of the material. The value of n is 1/2 or 2 depending upon whether the transition from valence to conduction band is direct or indirect.

The extrapolation of the linear part in figure 6 that meets the abscissa gives the values of the gap energy E_g of these products between 3.21 and 5.10 eV as are listed above in the table II. The best values were found with nanohybrid of 180°C growth temperature with nanostructured particles cubes and spheres shape composed of $\text{Ni}(\text{HCO}_3)_2/\text{Graphene}$ composition.

Electrochemical Properties

The cyclic voltammetry (CV) tests were carried out in the potential range 0 to 0.65 V at increasing scan rates ranging from 5 to 100 mV.s^{-1} . Figure 7 shows the obtained CV voltammograms at a scan rate 5 mV.s^{-1} in this investigation where we have the current density measured as a function of the applied voltage via Hg/HgO reference electrode.

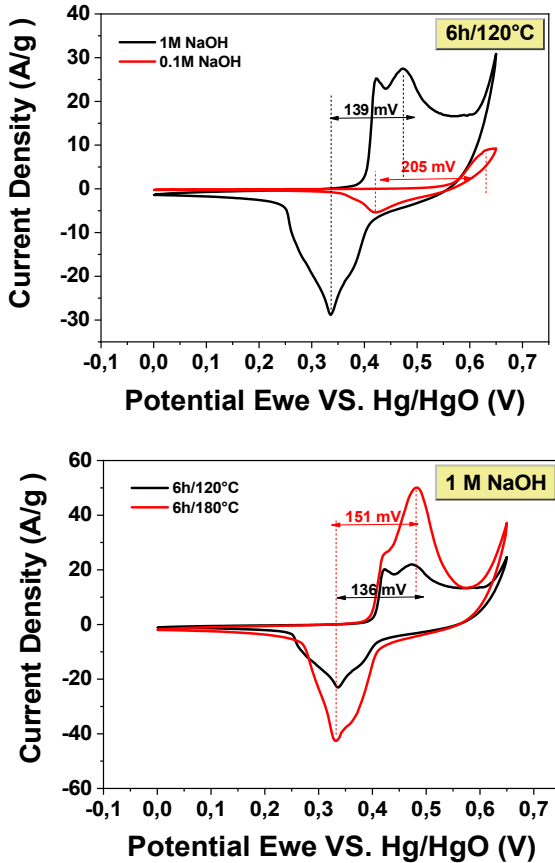
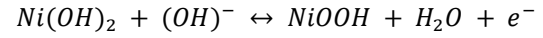


Fig. 7: Voltammograms (CV) of Ni/Graphene nanohybrid synthesized using hydrothermal method at two different conditions: electrolyte concentration and growth temperature effect.

These cyclic voltammetry curves clearly show a quasi-symmetric electrical response with $\Delta E_p = 136$ mV and 151 mV for obtained nanohybrids of 6h/120°C and 6h/180°C hydrothermal condition, respectively, thus proving the reversibility ($\Delta E_p < 200$ mV) of the electrochemical phenomenon in this potential range for both samples in 1M NaOH as generally reported in the literature [41]. The shape of these CV curves allows distinguishing the electrochemical mechanism involving these nanoproducs during the charge shift in the used aqueous electrolyte. Accordingly, they

represent cathodic peaks for the reduction process (bottom) and anodic peaks for the oxidation process (top); which consequently confirm an oxidation-reduction (Redox) mechanism. This confirms so a pseudo-capacitive or Faradic mechanism specific to transition metal electroactive materials, as reported in the storage energy literature [41]. Moreover, we confirm this mechanism via the peaks existence of the following redox reaction:



In addition, with increasing scan rate, we clearly can see also similar CV responses shape where anodic peaks shift positively, while their cathodic peaks shift negatively due to the internal resistance of the electrode that arises from the diffusion of the electrolyte ions within the electrode [49]. This phenomena was be accompanied with increasing current densities revealing higher charge storage; but this low shifting indicate the excellent EC reversibility and outstanding high-rate performance as found generally in literature.

The gravimetric specific capacitance (C_s in F.g^{-1}) values were calculated according to the following equation [44] :

$$C_s = \frac{\int I dV}{m v \Delta V}$$

where m is the mass of the loaded active material (in g), n represents the scan rate (in mV.s^{-1}), ΔV ($V_c - V_a$) refer to the potential window between high and low potential limit of the CV curve, $\int I dV$ is the integrated area under the curve for the cathodic current of the CV curve (in mA.V)

Finally, these electrochemical CV results were also used to estimate the very interesting specific capacity values for each product that is around 1863 and 253 F.g^{-1} for nanohybrid obtained at 6h/120°C in two different NaOH electrolyte concentrations 1 and 0.1 M, respectively. However, for a fixed 1 M NaOH aqueous electrolyte concentration, these two nanohybrids obtained at 120°C and 180°C gave specific capacity values around 1863 and 2981 F.g^{-1} , respectively. Consequently, they show very attractive specific capacity more in the case of $\text{Ni}(\text{HCO}_3)_2/\text{Graphene}$ nanohybrid based nanostructured cubes or spheres particles with low gap energy proved by previous optical properties. This experient has proved the efficiency of carbonate ions as well as the nanohybrid composition basing on transition metal and carbon at nanoscale.

IV. CONCLUSION

Simple and low cost hydrothermal method was employed to synthesize Ni hydroxide and Ni hydrogen carbonate and their nanohybrids based on Graphene nanosheets. The as-prepared products are studied by different characterization techniques to determine their physico-chemical properties. The results of the crystallographic analysis using XRD technique showed that these nanomaterials have quasi-amorphous nanostructures type hydroxide and carbonate at 6h/120°C and 6h/180°C, respectively. Then, this structural information is confirmed through their FTIR spectra by indicating the existence of the characteristic bonds such as Ni-OH and -OH groups linked to the existence of water in the case of the product with pure Ni mono-hydroxide kind, as well as added bonds of carbonate CO_3^{2-} in Ni hydrogen carbonate with C=O in the case of their nanohybrids basing on the Graphene existence (precisely Graphene oxide GO).

Moreover, the electrochemical measurements through their CV tests in two different NaOH aqueous electrolyte concentrations (1 and 0.1 M) show a very interesting specific capacities around 1863 and 253 F.g⁻¹ for nanohybrid obtained at 6h/120°C, respectively. However, at fixed 1 M NaOH electrolyte concentration, both nanohybrids obtained at 120°C and 180°C gave specific capacity values around 1863 F.g⁻¹ and 2981 F.g⁻¹, respectively, proving in consequence the role added of CO₃²⁻ and OH ions in electrochemical performance improvement besides metal transition nanocubes and Graphene conductivity.

ACKNOWLEDGMENT

We express our gratitude and sincere thanks to Prof. D. BEGIN and Prof. I. Janowska group's (ICPEES, Strasbourg) for performing the characterization experiment. The authors also thank the Algerian minister program and Directorate General for Scientific Research and Technological Development (DGRSDT) from Algeria for financial support.

REFERENCES

- [1] M.S. Dresselhaus, I. Thomas, "Alternative energy technologies", *Nature*, vol. 414, pp. 332-337, 2001. [doi: 10.1038/35104599](https://doi.org/10.1038/35104599)
- [2] D.A. Lashof, D.R. Ahuja, "Relative contributions of greenhouse gas emissions to global warming", *Nature*, vol. 344, pp. 529-531, 1990. <https://doi.org/10.1038/344529a0>
- [3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, "Dye-sensitized solar cells", *Chemical reviews*, vol. 110 (11), pp. 6595-6663, 2010. <https://doi.org/10.1021/cr900356p>
- [4] C. An, Y. Zhang, H. Guo, Y. Wang, "Metal oxide-based supercapacitors: progress and perspectives", *Nanoscale Advances*, vol. 1, pp. 4644-4658, 2019. <https://doi.org/10.1039/C9NA00543A>
- [5] M. Winter, R.J. Brodd, "What are batteries, fuel cells, and supercapacitors?", *Chemical reviews*, vol. 104, pp. 4245-4270, 2004. <https://doi.org/10.1021/cr020730k>
- [6] A.G. Pandolfo, A.F. Hollenkamp, "Carbon properties and their role in supercapacitors", *Journal of power sources*, vol. 157, pp. 11-27, 2006. <https://doi.org/10.1016/j.jpowsour.2006.02.065>
- [7] P.J. Hall, M. Mirzaei, S.I. Fletcher, F.B. Sillars, A.J. Rennie, G.O. Shitta-Bey, G. Wilson, A. Cruden, R. Carter, "Energy storage in electrochemical capacitors: designing functional materials to improve performance", *Energy & Environmental Science*, vol. 3, pp. 1238-1251, 2010. <https://doi.org/10.1039/C0EE00004C>
- [8] Y. Zhu, S. Murali, M.D. Stoller, K.J. Ganesh, W. Cai, P.J. Ferreira, A. Pirkle, R.M. Wallace, K.A. Cychosz, M. Thommes, "Carbon-based supercapacitors produced by activation of graphene", *science*, vol. 332, pp. 1537-1541, 2011. [doi: 10.1126/science.1200770](https://doi.org/10.1126/science.1200770)
- [9] G. Santhosh, G. Nayaka, A.S. Bhatt, "Ultrahigh capacitance of NiCo₂O₄/CeO₂ mixed metal oxide material for supercapacitor applications", *Journal of Alloys and Compounds*, vol. 899, pp. 163312, 2022. <https://doi.org/10.1016/j.jallcom.2021.163312>
- [10] Y. Zhang, L. Li, H. Su, W. Huang, X. Dong, "Binary metal oxide: advanced energy storage materials in supercapacitors", *Journal of Materials Chemistry A*, vol. 3, pp. 43-59, 2015. <https://doi.org/10.1039/C4TA04996A>
- [11] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J.P. Ferraris, "Conducting polymers as active materials in electrochemical capacitors", *Journal of power sources*, vol. 47, no 1-2, pp. 89-107, 1994. [https://doi.org/10.1016/0378-7753\(94\)80053-7](https://doi.org/10.1016/0378-7753(94)80053-7)
- [12] A. Eftekhari, L. Li, Y. Yang, "Polyaniline supercapacitors", *Journal of Power Sources*, vol. 347, pp. 86-107, 2017. <https://doi.org/10.1016/j.jpowsour.2017.02.054>
- [13] H. Dai, R. Li, S. Su, Y. Cui, Y. Lin, L. Zhang, X. Zhu, "Preparation and characterization of PANI/MWCNT/RGO ternary composites as electrode materials for supercapacitors", *Journal of Electronic Materials*, vol. 51, no 3, pp. 1409-1420, 2022. <https://doi.org/10.1007/s11664-021-09421-6>
- [14] B. De, S. Banerjee, K.D. Verma, T. Pal, P. Manna, K.K. Kar, Carbon nanotube as electrode materials for supercapacitors, in: *Handbook of nanocomposites supercapacitor materials II*, Springer, pp. 229-243, 2020. https://doi.org/10.1007/978-3-030-52359-6_9
- [15] S. Hu, S. Zhang, N. Pan, Y.-L. Hsieh, "High energy density supercapacitors from lignin derived submicron activated carbon fibers in aqueous electrolytes", *Journal of Power Sources*, vol. 270, pp. 106-112, 2014. <https://doi.org/10.1016/j.jpowsour.2014.07.063>
- [16] J. Chen, J. Xie, C.Q. Jia, C. Song, J. Hu, H. Li, "Economic preparation of high-performance activated carbon fiber papers as self-supporting supercapacitor electrodes", *Chemical Engineering Journal*, vol. 450, pp. 137938, 2022. <https://doi.org/10.1016/j.cej.2022.137938>
- [17] R. Kötz, M. Carlen, "Principles and applications of electrochemical capacitors", *Electrochimica Acta*, vol. 45, no 15-16, pp. 2483-2498, 2000. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6)
- [18] T. Nguyen, M.d.F. Montemor, "Metal oxide and hydroxide-based aqueous supercapacitors: from charge storage mechanisms and functional electrode engineering to need-tailored devices", *Advanced Science*, vol. 6, no 9, pp. 1801797, 2019. <https://doi.org/10.1002/advs.201801797>
- [19] C. Lee, X. Wei, J.W. Kysar, J. Hone, "Measurement of the elastic properties and intrinsic strength of monolayer graphene", *science*, vol. 321, no 5887, pp. 385-388, 2008. <https://doi.org/10.1126/science.1157996>
- [20] X. Huang, X. Qi, F. Boey, H. Zhang, "Graphene-based composites", *Chemical Society Reviews*, vol. 41, no 2, pp. 666-686, 2012. <https://doi.org/10.1039/C1CS15078B>
- [21] G. Eda, G. Fanchini, M. Chhowalla, "Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material", *Nature nanotechnology*, vol. 3, no 5, pp. 270-274, 2008. <https://doi.org/10.1038/nnano.2008.83>
- [22] L. Gomez De Arco, Y. Zhang, C.W. Schlenker, K. Ryu, M.E. Thompson, C. Zhou, "Continuous, highly flexible, and transparent graphene films by chemical vapor deposition for organic photovoltaics", *ACS nano*, vol. 4, no 5, pp. 2865-2873, 2010. <https://doi.org/10.1021/nn901587x>
- [23] R. Raccichini, A. Varzi, S. Passerini, B. Scrosati, "The role of graphene for electrochemical energy storage", *Nature materials*, vol. 14, no 3, pp. 271-279, 2015. <https://doi.org/10.1038/nmat4170>
- [24] S. Vivekchand, C.S. Rout, K. Subrahmanyam, A. Govindaraj, C.N.R. Rao, "Graphene-based electrochemical supercapacitors", *Journal of Chemical Sciences*, vol. 120, no 1, pp. 9-13, 2008. <https://doi.org/10.1007/s12039-008-0002-7>
- [25] M.D. Stoller, S. Park, Y. Zhu, J. An, R.S. Ruoff, "Graphene-based ultracapacitors", *Nano letters*, vol. 8, no 10, pp. 3498-3502, 2008. <https://doi.org/10.1021/nl802558y>
- [26] S. Vazquez, S.M. Lukic, E. Galvan, L.G. Franquelo, J.M. Carrasco, "Energy storage systems for transport and grid applications", *IEEE Transactions on industrial electronics*, vol. 57, no 12, pp. 3881-3895, 2010. <https://doi.org/10.1109/TIE.2010.2076414>
- [27] G. Zhang, X. Xiao, B. Li, P. Gu, H. Xue, H. Pang, "Transition metal oxides with one-dimensional/one-dimensional-analogue nanostructures for advanced supercapacitors", *Journal of Materials Chemistry A*, vol. 5, no 18, pp. 8155-8186, 2017. <https://doi.org/10.1039/C7TA02454A>
- [28] R. Liang, Y. Du, P. Xiao, J. Cheng, S. Yuan, Y. Chen, J. Yuan, J. Chen, "Transition metal oxide electrode materials for supercapacitors: a review of recent developments", *Nanomaterials*, vol. 11, no 5, pp. 1248, 2021. <https://doi.org/10.3390/nano11051248>
- [29] X. Li, D. Du, Y. Zhang, W. Xing, Q. Xue, Z. Yan, "Layered double hydroxides toward high-performance supercapacitors", *Journal of Materials Chemistry A*, vol. 5, no 30, pp. 15460-15485, 2017. <https://doi.org/10.1039/C7TA04001F>
- [30] L. Zhang, D. Shi, T. Liu, M. Jaroniec, J. Yu, "Nickel-based materials for supercapacitors", *Materials Today*, vol. 25, pp. 35-65, 2019. <https://doi.org/10.1016/j.mattod.2018.11.002>
- [31] M. Aghazadeh, M. Ghaemi, B. Sabour, S. Dalvand, "Electrochemical preparation of α-Ni (OH)₂ ultrafine nanoparticles for high-performance supercapacitors", *Journal of Solid State Electrochemistry*, vol. 18, no 6, pp. 1569-1584, 2014. <https://doi.org/10.1007/s10008-014-2381-7>
- [32] C. An, Y. Zhang, H. Guo, Y. Wang, "Metal oxide-based supercapacitors: progress and perspectives", *Nanoscale Advances*, vol. 1, no 12, pp. 4644-4658, 2019. <https://doi.org/10.1039/C9NA00543A>
- [33] T. Nguyen, M. D. F. Montemor, "Metal oxide and hydroxide-based aqueous supercapacitors: from charge storage mechanisms and functional electrode engineering to need-tailored devices". *Advanced Science*, vol. 6, no 9, pp. 1801797, 2019. <https://doi.org/10.1002/advs.201801797>
- [34] C. Jiang, B. Zhao, J. Cheng, J. Li, H. Zhang, Z. Tang, J. Yang, "Hydrothermal synthesis of Ni(OH)₂ nanoflakes on 3D graphene foam for high-performance supercapacitors", *Electrochimica Acta*, vol. 173, pp. 399-407, 2015. <https://doi.org/10.1016/j.electacta.2015.05.081>
- [35] H. Wang, Y. Song, W. Liu, L. Yan, "Three dimensional Ni (OH)₂/rGO hydrogel as binder-free electrode for asymmetric supercapacitor", *Journal of Alloys and Compounds*, vol. 735, pp. 2428-2435, 2018. <https://doi.org/10.1016/j.jallcom.2017.11.358>
- [36] J. Liu, Y. Wang, R. Hu, H.A. Munir, H. Liu, "High-performance supercapacitor electrode based on 3D rose-like β-Ni (OH)₂/rGO nanohybrid", *Journal of Physics and Chemistry of Solids*, vol. 138, pp. 109297, 2020. <https://doi.org/10.1016/j.jpcs.2019.109297>
- [37] P.G. Choi, K. Kim, Y. Masuda, "Porous NiO Nanosheet Based High Sensitivity Acetone Gas Sensor Capable of Parts-Per-Billion Level Detection", <https://dx.doi.org/10.2139/ssrn.4077548>
- [38] A.K. Patra, S.K. Kundu, D. Kim, A. Bhaumik, "Controlled Synthesis of a Hexagonal-Shaped NiO Nanocatalyst with Highly Reactive Facets

- (110) and Its Catalytic Activity”, Chem. Cat. Chem, vol. 7, no 5, pp. 791-798, 2015. <https://doi.org/10.1002/cctc.201402871>
- [39] Z. Gao, Z. Wang, J. Chang, L. Chen, D. Wu, F. Xu, X. Wang, K. Jiang, “Micelles directed preparation of ternary cobalt hydroxide carbonate nickel hydroxide-reduced graphene oxide composite porous nanowire arrays with superior faradic capacitance performance”, Journal of Colloid and Interface Science, Vol. 534, pp. 563–573, 2019. <https://doi.org/10.1016/j.jcis.2018.09.068>
- [40] R. Thangappan, S. Kalaiselvam, A. Elayaperumal, R. Jayavel, “Synthesis of graphene oxide/vanadium pentoxide composite nanofibers by electrospinning for supercapacitor applications”, Solid State Ionics, Vol. 268, pp. 321–325, 2014. <http://dx.doi.org/10.1016/j.ssi.2014.10.025>
- [41] X. Wu, X. Pang, X. An, X. Xie, “Kinetics and mechanism of formation of benzoin ethyl ether from benzaldehyde and ethanol using heterogeneous $\text{Ni}(\text{HCO}_3)_2$ as catalyst”, Progress in Reaction Kinetics and Mechanism, vol. 39, no 3, pp. 299-307, 2014. <https://doi.org/10.3184/146867814X14043731662783>
- [42] F. Kong, X. He, J. Chen, S. Tao, B. Qian, X. Jiang, H. Luo, “Hierarchical $\text{Ni}(\text{HCO}_3)_2$ Nanosheets Anchored on Carbon Nanofibers as Binder-Free Anodes for Lithium-Ion Batteries”, Energy Technology, vol. 7, no 6, pp. 1900094, 2019. <https://doi.org/10.1002/ente.201900094>
- [43] R. Siburian, H. Sihotang, S. Lumban Raja, M. Supeno And C. Simanjuntak, “New Route to Synthesize of Graphene Nano Sheets”, Orient. J. Chem., Vol. 34(1), 182-187 (2018). DOI: [10.13005/ojc/340120](https://doi.org/10.13005/ojc/340120).
- [44] O. Guellati, A. Harat, D. Momodu, J. Dangbegnon, T. Romero, D. Begin, C. Pham-Huu, N. Manyala, M. Guerioune, “Electrochemical measurements of 1D/2D/3D Ni-Co bi-phase mesoporousnanohybrids synthesized using free-template hydrothermal method”, Electrochimica Acta, vol. 275, pp. 155-171, 2018. <https://doi.org/10.1016/j.electacta.2018.04.112>
- [45] Z. Liu, R. Ma, M. Osada, K. Takada, T. Sasaki, “Selective and controlled synthesis of α - and β -cobalt hydroxides in highly developed hexagonal platelets”, Journal of the American Chemical Society, vol. 127, no 40, pp. 13869-13874, 2005. <https://doi.org/10.1021/ja0523338>
- [46] P. Lokhande, U. Chavan, “Nanostructured $\text{Ni}(\text{OH})_2/\text{rGO}$ composite chemically deposited on Ni foam for high performance of supercapacitor applications”, Materials Science for Energy Technologies, vol. 2, no 1, pp. 52-56, 2019. <https://doi.org/10.1016/j.msset.2018.10.003>
- [47] N. Habib, O. Guellati, A. Harat, A. Nait-Merzoug, J. El Haskouri, D. Momodu, N. Manyala, D. Begin, M. Guerioune, “Ni–Zn hydroxide-based bi-phase multiscale porous nanohybrids: physico-chemical properties”, Applied Nanoscience, vol. 10, no 8, pp. 2467-2477, 2020. <https://doi.org/10.1007/s13204-019-01062-w>
- [48] J. Tauc, Optical properties and electronic structure of amorphous Ge and Si, Materials research bulletin, vol. 3, no 1, pp. 37-46, 1968. [https://doi.org/10.1016/0025-5408\(68\)90023-8](https://doi.org/10.1016/0025-5408(68)90023-8)
- [49] M.M.M. Mohammed, A.G. Abd-Elrahim, D.-M. Chun, One-step deposition of a $\text{Ni}(\text{OH})_2$ -graphene hybrid prepared by vacuum kinetic spray for high energy density hybrid supercapacitor, Materials Chemistry and Physics, vol. 244, pp. 122701, 2020. <https://doi.org/10.1016/j.matchemphys.2020.122701>



Ikram DJEBABLIA Phd in Applied physics, Domain of research : Energy storage (experimental and theoretical).



Ouannassa GUELLATI, researcher in LEREC laboratory in Algeria and Teacher at Souk-Ahras University, has completed her PhD from Badji-Mokhtar University of Annaba 2013, Algeria on production of Carbon nanotube (CNTs) using CCVD technique and their functionalization and macronisation. She has published 23 papers in reputed journals with high impact factor. She has presented in september 2020 her university habilitation at Annaba University. She is current reviewer in Nanoscale Research Letters and Materials Science and Engineering B – Journal Elsevier. Actually, she is working on the production of smart nanomaterials like transition metal hydroxides, oxides and nanostructured polyaniline and their nanocomposites / nanohybrids with CNTs and/or Graphene as well as mesoporous Biochars for energy storage, environment and Biosensing application. She is working in collaboration with ICPEES at ECPM, Strasbourg – France, IMS at University of Valencia – Spain, CES at Namur University, SARChI Chair in Carbon Technology and Materials at Pretoria University, South Africa and DISAT - Politecnico di Torino, Italy.

Physico-Chemical Properties of Three Synthesized Carbonaceous Nanomaterials (CNTs, GO, Biochar) for Perspective Application: Water / Soil Treatment and Energy Storage

Hanene Araissia, Ouanassa Guellati, Fatma Abbaci, Aicha Harat, Jamal El-Haskouri, Dominique Begin,

Mohamed Guerioune and Aissa Nait-Merzoug

Abstract– Nanotechnology has a more than important role in deducing the materials' structure, especially carbon-based nanomaterials, including determining their properties and consequently their application field, such as: energy storage, environmental protection, biosensing and soil treatment. In this investigation, we report a comparison of three kinds of nanostructured carbon based smart nanomaterials synthesized at different dimension (1D, 2D and 3D) using physico-chemical growth processes. These carbonaceous products have been characterized in order to identify their attractive properties using different techniques, such as XRD, FT-IR, TGA/DTA, FESEM microscopy, Raman and XPS spectroscopy. These obtained nanostructured carbon have shown structural forms in the case of MWNTs and graphene type having 1D and 2D configuration, respectively, as well as an amorphous form in the case of biochar having 3D porous configuration which contains less cohesive bonds than graphene and MWNTs. These two structured ones have a much more solid and cohesive structure thanks to the strength of their carbon bonds and their graphitization rate is proved from their Raman and XPS-C1s analysis spectra. Moreover, they have shown very interesting characteristics especially their specific surface area in the range 150-2400 m²/g and functional groups; which open up a wide field of application especially environmental protection and biosensing.

Keywords– Carbonaceous nanomaterials, Carbon nanotube (CNTs), graphene, biochar, Environmental protection Soil treatment.

I. INTRODUCTION

Humanity lives today under serious threats which negatively affect its various activities. Pollution can be considered as the first concern and the main cause of problems related to most areas including health and economics. So, it is necessary to rely on natural, renewable and environmental friendly sources as the main solution to these issues. This is in parallel with the work on the technological development of energy storage, depollution, sensing, which prompted the world to fight against these anomalies thanks to the emergence of Nanosciences and Nanotechnologies [1-5].

Nanotechnology is most important at the forefront of today and exciting fields, such as materials science, engineering, biotechnology, agriculture, etc. It has given great hope for scientific revolutions in the near future that have change the direction of technology in many application fields. The concept of nanotechnology is based on the assumption that smaller particles than one hundred nanometers give the material new attractive properties and new behaviors which express new physical and chemical concepts [1, 6, 7].

Nanotechnology has opened the way to study the matter shapes and the components at the nano level (atomic scale). Moreover, nanomaterials are one of the main nanotechnology products that can be categorized into three types: one-dimensional (1D), two dimensional (2D) and three dimensional (3D) where each of these materials exhibits unique properties based on its particular characteristics [8, 9]. Among the most important of them, we mentioned the carbon nanotubes (CNTs) which are composed either of a single sheet of graphene (SWNTs) rolled up on itself in such a way to form a cylinder (1D) with a diameter between 0.4 and 3 nm; or multi walled nanotubes (MWNTs) with inter-tubes distance 0.34 nm [10-14]. Then, we find graphene which is the thinnest and strongest material known to date. It is a 2D crystalline sheet, as the first studied crystal of allotropy, based on hexagons of carbon one atom thick in sp² hybridation in a honeycomb structure, at the origin of Graphite. More precisely, FLG (Few Layer Graphene) have emerged as potential platforms for exploring novel and unique properties no found in other materials due to their planar geometry and their related in-plane propagation properties [15]. Finally, biochar is the solid part obtained through pyrolysis of the organic matter biomass in the absence of oxygen [16, 17]. It possesses amorphous structure in 3D configuration with interesting contact specific surface [16, 18].

Manuscript received October 12, 2022; revised July 1, 2023.

H. Araissia is with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA. (e-mail: araisiahane@gmail.com)
O. Guellati and A. Nait-Merzoug are with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA and LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: guellati23@yahoo.fr and abenlala@yahoo.fr)

F. Abbaci, A. Harat and M. Guerioune are with LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mail: fatmaabbaci@yahoo.fr, harat_aicha@yahoo.fr and mguerioune@yahoo.fr)

J. El-Haskouri is with Institute of Materials Science, University of Valencia, C/ Catedrático José Beltrán, 2, CP 46980 Paterna, Valencia – SPAIN. (email: jamal.haskouri@uv.es)

D. Begin is with ICPEES Institute, ECPM - CNRS, UdS, 25 Rue Becquerel, 67087 Strasbourg, FRANCE. (email: dominique.begin@unistra.fr)

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.160

In this paper, we present the successful synthesized products based on three kinds of carbon-based nanomaterials (biochar, MWNTs and graphene) and the comparison between them using very specific characterization techniques to deduce their attractive physico-chemical properties. They have shown very interesting characteristics basing on specific surface area and functional groups which open up to a wide field of their application as smart nanomaterial.

II. EXPERIMENTAL PROCEDURE

A. Carbonaceous nanomaterials synthesis

Biochar production: Activated biochar from potato peels biomass was prepared through double pyrolysis process basing on chemical and physical aspect. At first, the potato peels, with a thickness not more than 2 mm, were cleaned and natural dried for 48 hours. After that, the dried biomass was ground using Coffee grinder to obtain very fine particles. Then, 20 g of this dried matter with and without oxidant agent was placed in a ceramic boat and transferred onto horizontal quartz reactor inside the cylinder furnace under an inert N₂ atmosphere (200 ml/min). Therefore, the pyrolysis is carried out via a simple thermal cycle with heating speed 5°C.min⁻¹ and carbonization temperature of 600 °C during 2 hours. Consequently, the produced activated biochar was immersed in 2 M HCl for 24 h to remove any inorganic salts and then washed several times with distilled water until a neutral pH achievement [16].

MWNTs par CCVD: The MWNTs studied in this investigation were synthesized using catalytic CVD technique over using Fe/Al₂O₃ catalyst support at 750 °C growth temperature during 1 hour with acetylene and nitrogen as carbon source and carrier gas, respectively. After that, they were purified and functionalized through heated acid treatment (HCl : HNO₃ = 1:3) at 80 °C for 2 hours, then washed and filtered several times with deionized water until no detected residual acid. Finally, they were dried at 80 °C for 20 hours [10].

Graphene exfoliation: Direct liquid-phase exfoliation of layered materials by means of ultrasound was used to synthesis few layered graphene (FLG) using Janowska team process [19].

B. Characterization techniques

For structural identification, these carbonaceous materials were characterized with powder X-ray diffraction (PXRD) (PAN analytical XPert PRO Bragg-Brentano diffractometer) equipped with CuK α ($\lambda = 1.540598$ Å) where the analysis was performed with a step size of 0.017°.min⁻¹ at room temperature in the 2 θ range [5 - 90°]. The relative crystallinity degree (CD) was estimated using following equation [16], where A_c and A_a are the area of the crystalline and amorphous peaks, respectively, in the XRD diffractogram. $CD (\%) = \frac{A_c}{(A_c + A_a)}$.

Moreover, the FT-IR technique is an important tool also to identify the chemical binding of formed functional groups. We have used an analyzed by a Bruker Vertex 77 v spectrometer with a 4 cm⁻¹ resolution controlled with an Opus software in the wave number range of 4000 – 400 cm⁻¹. In addition, Raman analysis was used to identify quantitatively and qualitatively the carbon-based nanomaterials in order to understand their crystalline/defect nature. So, we have carried out this analysis on a Horiba Jobin Yvon Lab – Ram Aramis confocal Raman Spectrometer recorded using 532 nm laser excitation with 0.33 mW power. Thermal analysis measurements have been also carried out using the TGA/DTA technique which gives qualitative information on the products composition as well as their percentage as quantitative estimation. Therefore, we have used the TGA 550-TA instrument with a heating speed of 10 °C.min⁻¹ from room temperature to 1000 °C under an air

atmosphere. Besides, the surface morphology of these products was analyzed using a Field Emission Scanning Electron Microscopy “FESEM microscopy” (JEOL JSM-7500 F Model) equipped with a secondary electrons detector with 15 kV accelerating voltage showing the textural morphology. The specific surface area (SSA), total pore volume and pore size distribution as important textural characteristic for ulterior use of produced carbonaceous nanomaterials were carried out via N₂ adsorption-desorption isotherm (at 77 °K liq-N₂) using ASap2020 Micrometrics. Also, the Barrett-Joyner-Halenda (BJH) and Density Functional Theory (DFT) methods were used automatically to provide a micro- and meso-scope pores distribution, respectively. At last, X-ray induced photoelectron spectroscopy (XPS) is a method of surface analysis which allows to thoroughly determine the chemical composition and binding of the studied products. In this investigation, we focalize on the functional groups information and the bonds nature to follow the chemical surface modifications. So, we have used Scientific K-Alpha Spectrophotometer by monochromatic Al K α radiation (1486.6 eV). First, a wide sweep scan was carried out from 0 to 1400 eV as survey scan to define the main element present in the product. After that, the main peak precise analysis to obtain base-level spectra has been calibrated with respect to graphite carbon where C1s was leveled at 284.6 eV. Composition products and their main peaks deconvolution for all reached XPS spectra were performed using Avantage software where the curves fitting has been done basing on mixed Gaussian/Lorentzian peak shape (by 0.3).

III. RESULTS AND DISCUSSION

Structural Characteristics

Figure 1 illustrates the typical XRD patterns of synthesized biochar and MWNTs at optimized conditions. This structural identification of these products through their characteristic peaks using JCPDS reference cards allows differentiating them from a structural aspect point of view.

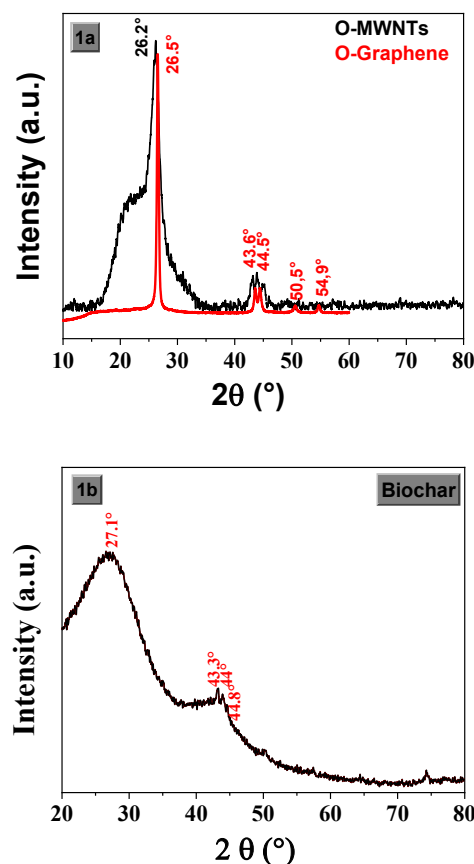


Fig. 1: XRD diffractograms of two different carbonaceous nanomaterial: MWNTs and biochar.

Therefore, the XRD spectrum (Fig. 1a) confirms the formation of carbon nanotubes "CNTs" with an hexagonal structure according to the JCPDS reference card N° [00-041-1487] through narrow shape peaks located at 26.3° , 43.2° , 43.9° and 45° corresponding respectively the following crystalline plans (002), (100), (101) and (101) [10]. Also, the more intense diffraction peak was observed at around 26.3° (MWNTs) - 26.5° (graphene) corresponding to (002) plan with an interlayer spacing of about 0.34 nm [20].

However, the spectrum in figure 1b is characterized by almost the same 2θ positions with some shifts confirming the carbon composition but with broader shape aspect than those of CNTs indicating the product semi-crystalline state [16].

So, this structural identification confirms clearly the amorphous aspect of produced biochar in comparison to structural one (Fig. 1a) that was proved from their estimated crystallinity degree (CD). We found MWNTs with more crystallinity (42 %) than biochar (5.6 %) justifying consequently more the below results.

To identify more exactly the main existing chemical bands inside these products, figure 2 represents their obtained FT-IR spectra to reveal their functional groups in the range $[4000 - 400 \text{ cm}^{-1}]$. Generally, the types of chemical binding can be classified according to their wave number values. In these products focalizing on the strong broad peaks, we can observe that in the case of MWNTs, the main binding bands are assigned to : 1553 cm^{-1} (C=O / C-O), $1648-1694 \text{ cm}^{-1}$ (C=C), $3668-3855 \text{ cm}^{-1}$ (O-H) and $2850-2926 \text{ cm}^{-1}$ (CH_3/CH_2) [20, 21]. Whereas, in the case of biochar, the essential bands are found at 3163 cm^{-1} (COOH and -COH), 1586 cm^{-1} (C=O), $1442-1350 \text{ cm}^{-1}$ (carbonate ions) and $2143-2035 \text{ cm}^{-1}$ (O-H).

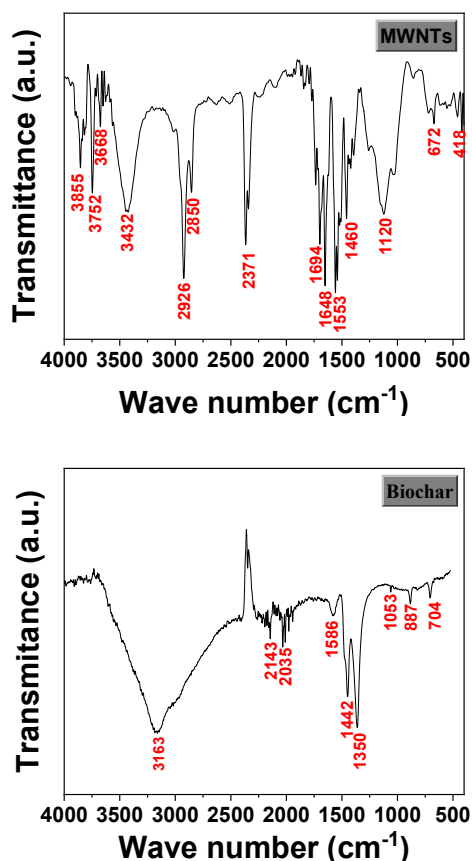


Fig. 2: FT-IR spectra of two different carbonaceous nanomaterial: MWNTs and biochar.

Thereby, according to these differences in bonds and consequently the nature of the atoms binding, we can easily

deduce that MWNTs are more structured, rigid and coherent by comparing them with biochar product, which is much more based on the carbon-oxygen binding bands.

From their Raman analysis as shown in figure 3, we clearly observe the unique and essential two peaks "D" and "G" bands characterizing the carbonaceous materials [10, 22]. Usually, the G band peak gives the information on the graphitization degree through its position and intensity.

Its position is on a high Raman shift value in the case of crystallized nanomaterials with more graphitization which is found more with MWNTs (at 1596 cm^{-1}) and graphene (at 1580 cm^{-1}); while it is on its lower value (at 1566 cm^{-1}) in the case of amorphous carbon "biochar".

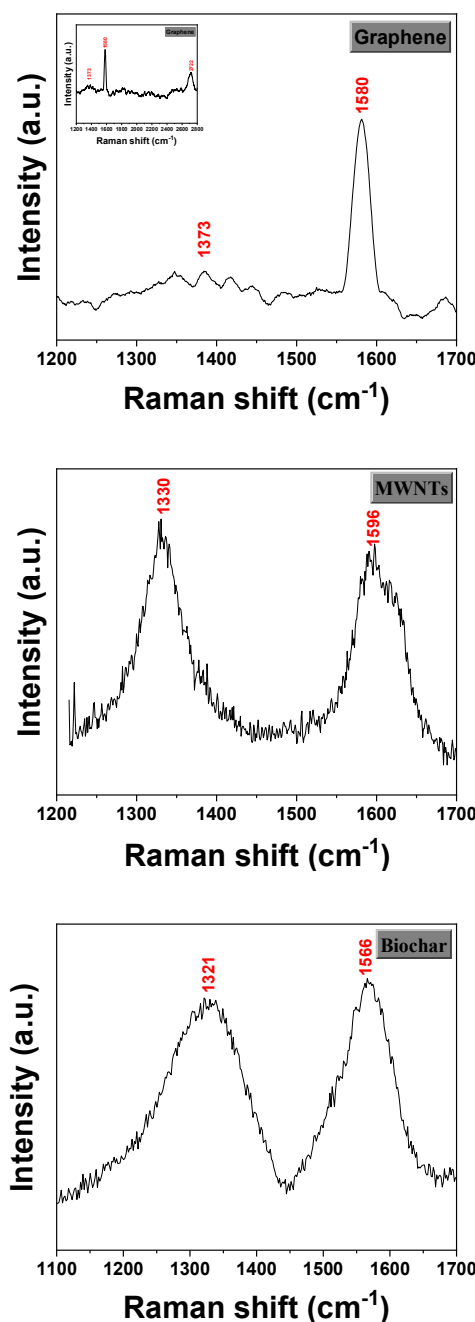


Fig. 3: Raman spectra of three kind of carbonaceous nanomaterials: graphene, MWNTs and biochar.

However, the D band peak shows the existence of defects in the carbon-based lattice of these products. Their values are found around 1321 cm^{-1} for the amorphous biochar and 1330 or 1384 cm^{-1} for the structured carbon like MWNTs and graphene, respectively [22]. According to these Raman spectra for three

studied carbon based products (MWNTs, graphene and biochar), we regroup in the following table I the deduced characteristics which confirm the structural/graphitization and defect difference.

Consequently, we clearly confirm that the much more graphitized product was the graphene and the MWNTs with estimated graphitization ratio I_G/I_D around 3.6 and 1.11, respectively. While, the disordered product was found with biochar proving by their estimated defect/graphitization I_D/I_G

Table. I

THE CHARACTERISTICS OF THE RAMAN PEAKS FOUND WITH THESE THREE KIND OF STUDIED CARBON-BASED NANOMATERIALS.

Samples	Position D (cm^{-1})	Position G (cm^{-1})	I_D/I_G	I_G/I_D
biochar	1321	1566	0.93	1.08
MWNTs	1330	1597	0.90	1.11
graphene	1384	1580	0.28	3.60

intensities ratio around 0.93. Moreover, this means that the graphene structure contains low impurities and defects compared to other studied carbonaceous nanomaterials (MWNTs and biochar) in this investigation [21, 23].

Therefore, from these intensities ratio, we recorded the graphitization following order graphene < MWNTs < biochar.

In addition, to estimate the graphene layers number we focalize on the D and 2D peaks as reported by V. Kumar work [15]. We found intensity ratio $I_D/I_G = 0,28$ and $I_{2D}/I_G = 0,54$ with 2D peak position at 2720 cm^{-1} ; which confirm the obtaining of 7 to 10 graphene layers proving hence Few Layer Graphene (FLG) based product.

Thermal Characteristics

In order to confirm our previous results, we have also used a thermal analysis (TA) technique which allows obtaining the thermal properties of these studied products. This technique gives qualitative/quantitative information on nature and composition of these products. Figure 4 illustrates two spectra of this carbonaceous nanomaterials thermal analysis. In the case of biochar, we observe that there are mainly four steps on the mass loss curve (TGA) and its equivalent in four oxidation peaks obtained on their derivative curves (DTA). These mass losses are characterized by their oxidation/combustion temperature found at: 30°C , 156°C , 411°C and 616°C , respectively. The first 12 wt.% loss was attributed to moisture loss; while the second loss was found with 8 wt.% which is due to the presence of adsorbed water. However, the third loss which is dominant with a percentage 65 wt.% presents the transformation and the combustion of their carbon-based skeleton into CO_2 . Finally, a last slight loss of 5 wt.% can be attributed to the presence of a structured carbon network. Therefore, the overall mass loss for this biochar as amorphous carbon based product is 90 wt.% with a residue of 10 wt.% due to a some residual traces of metals from the used biomass [16].

In the same way for the case of MWNTs as nanostructured carbon product, we observe that there are mainly two oxidation peaks found at 238°C and 615°C , corresponding to two losses of 5 wt.% and 90 wt.%, respectively. Consequently, the MWNTs possess a high purity and selectivity of 95% with residues of 5 wt.% that represent the used catalyst during their CCVD growth [10]. Finally, this thermal analysis allows to distinguish that MWNTs are more thermally resistant (with $T_{\text{oxy}} = 615^\circ\text{C}$) compared to biochar with a slightly lower oxidation temperature ($T_{\text{oxy}} = 412^\circ\text{C}$) proving the difference of their carbon network and the defect existence inside this network.

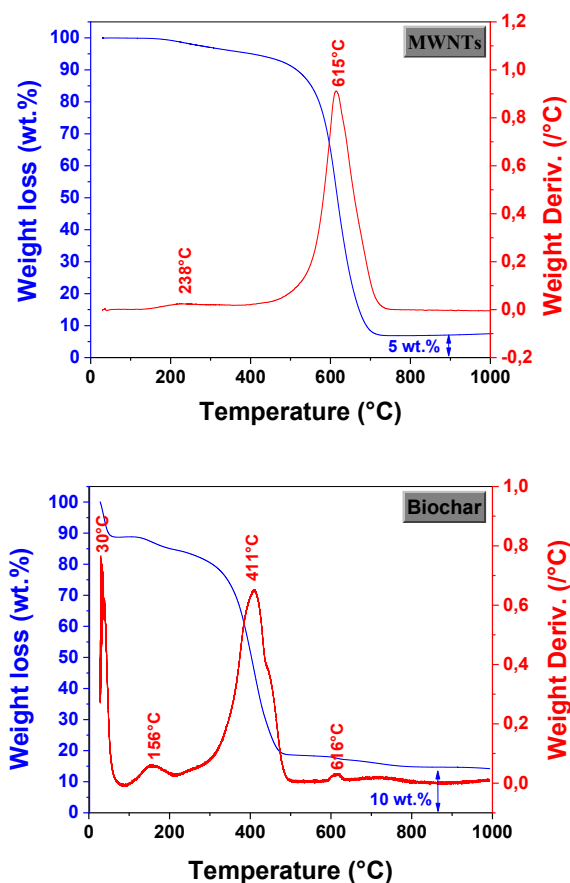


Fig. 4: Thermal analysis (TGA/DTA) of studied amorphous biochar and nanostructured MWNTs.

Morphological properties

FESEM microscopy is widely used to determine the surface morphology including the textural aspect of these carbonaceous products as illustrate in figure 5. Figure 5a shows the acquisition of one-dimensional (1D) tubular shapes with more or less homogeneous diameters between 20 and 50 nm. Their high resolution TEM (Fig. 5b) confirms that these nanotubes clearly are composed of multi walls cylinders which prove the Multi-Walled Nanotubes (MWNTs) formation. These MWNTs have average diameter around 20 nm with canal diameter around 10 nm and 14 walls possessing 0.36 nm calculated graphitic inter-crystallographic plan distance as shown inset figure 5b [10].

This kind of carbon nanotube is more useful for many application fields due to their contact surface which is around $150 \text{ m}^2/\text{g}$ that can be provided via the channels and voids between plans as well as their functional groups. However, figure 5c illustrates very thin 2D shape with a nanometric thickness. It confirms that the resulting graphene has a relatively smooth planar structure which tends to overlap. These graphene sheets have few layers as confirmed through the Raman results from 2D peak form.

In contrast to these structural carbons based products, biochar as represented in figure 5d, shows an amorphous spongy textural morphology of porous structure with relatively irregular surfaces containing many cracks (pores) [24]. This morphology gives it an interesting compositional textural aspect with a very interesting contact surface which found approximately around $2400 \text{ m}^2/\text{g}$ [16].

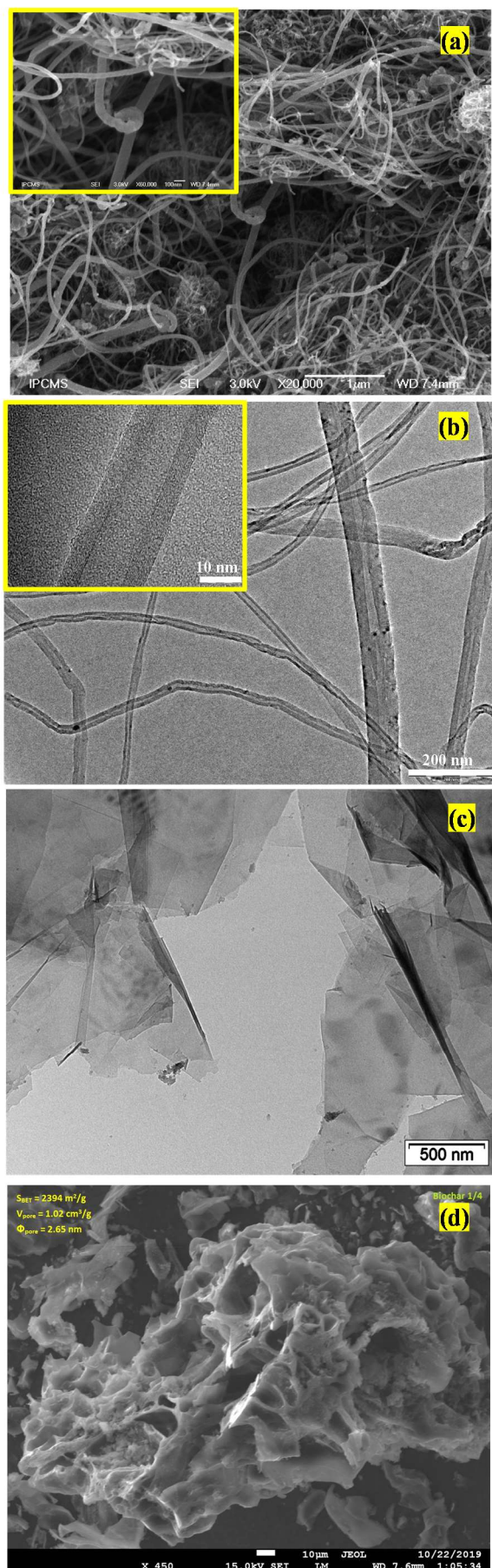


Fig. 5: High resolution FESEM and TEM micrographs for three kind of carbonaceous nanomaterial.

The above estimated specific surface area (contact surface) values of synthesized MWNTs and biochar have been performed through BET textural analysis as reported in figure 6. The N_2 adsorption-desorption isotherms (Fig. 6 left) can be

described as a combination of type I and type IV isotherms. Typically, these isotherms show an apparent hysteresis loop indicating the presence of mesopores accompanied with micropores which are confirmed by the pore size distribution inside products [16]. Moreover, as can be seen MWNTs are only based of mesoporous structure (pore size [2 – 50 nm]) while biochar have dominant micropores (< 2nm) with some mesopores around 4 nm, as shown in pore size BJH distribution curves (Fig. 6 right).

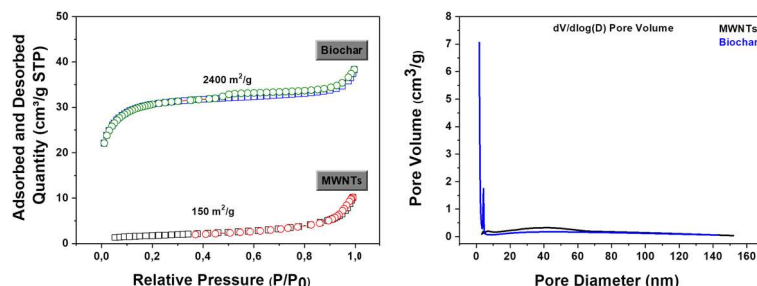


Fig. 6: N_2 adsorption-desorption isotherms (left) and their corresponding pore size distributions (right).

Spectroscopy characteristics

To more investigate the functional groups in these products, we have also used XPS technique allowing the surface chemical binding. Figure 7 represent the survey analysis of studied products showing the main chemical element with their atomic orbital: C_{1s} and O_{1s} at binding energy 284.6 and 532 eV, respectively [10, 12, 16]. Table II shows all the obtained binding energies from XPS for these three carbonaceous products (graphene, MWNTs and biochar). For further a more detailed investigation, we able used the obtained deconvolutions of these inhomogeneous peaks for main chemical elements such as C_{1s} and O_{1s} as shown in figure 7 (below). They showed exactly the functional groups found in these products clarifying consequently the previous results.

For the chemical bonds at the C_{1s} level, we observe in these carbon-based nanomaterials, whether in the amorphous (biochar) or in crystalline (MWNTs and graphene) carbonaceous form, the presence of five chemical bonds with different concentrations depending to product type, such as $C=C$ (sp^2) has a binding energy around 284.5 eV which is the strongest for the three products, accompanied with $C-C$ (283 eV), $C-O$ (285-286 eV), $C=O$ (287 eV), $O-CO$ (288-289 eV) and $O-C=O$ (290 eV) [25].

Table. II
THE MAIN CHEMICAL ELEMENTS MAKING UP THESE STUDIED CARBON-BASED NANOMATERIALS.

Sample	Binding energy (eV)	Element	C_{1s} (at.%)	O_{1s} (at.%)
graphene	284.4	C_{1s}	90	10
	532.5	O_{1s}		
	978	OKL ₂₃ L ₂₃		
	1225	CKL ₂₃ L ₂₃		
MWNTs	284.6	C_{1s}	87	6
	533.4	O_{1s}		
	981	OKL ₂₃ L ₂₃		
biochar	284.5	C_{1s}	63	37
	530.5	O_{1s}		
	978	OKL ₂₃ L ₂₃		

Otherwise with regard to the O_{1s} level, we indicate for MWNTs and graphene the dominant presence of $O-C$ / $C-O-C$ chemical bond level found around 532 eV with other secondary chemical bonds, like: $O=C$ / $O-C=O$ and the adsorbed water due to the storage effect.

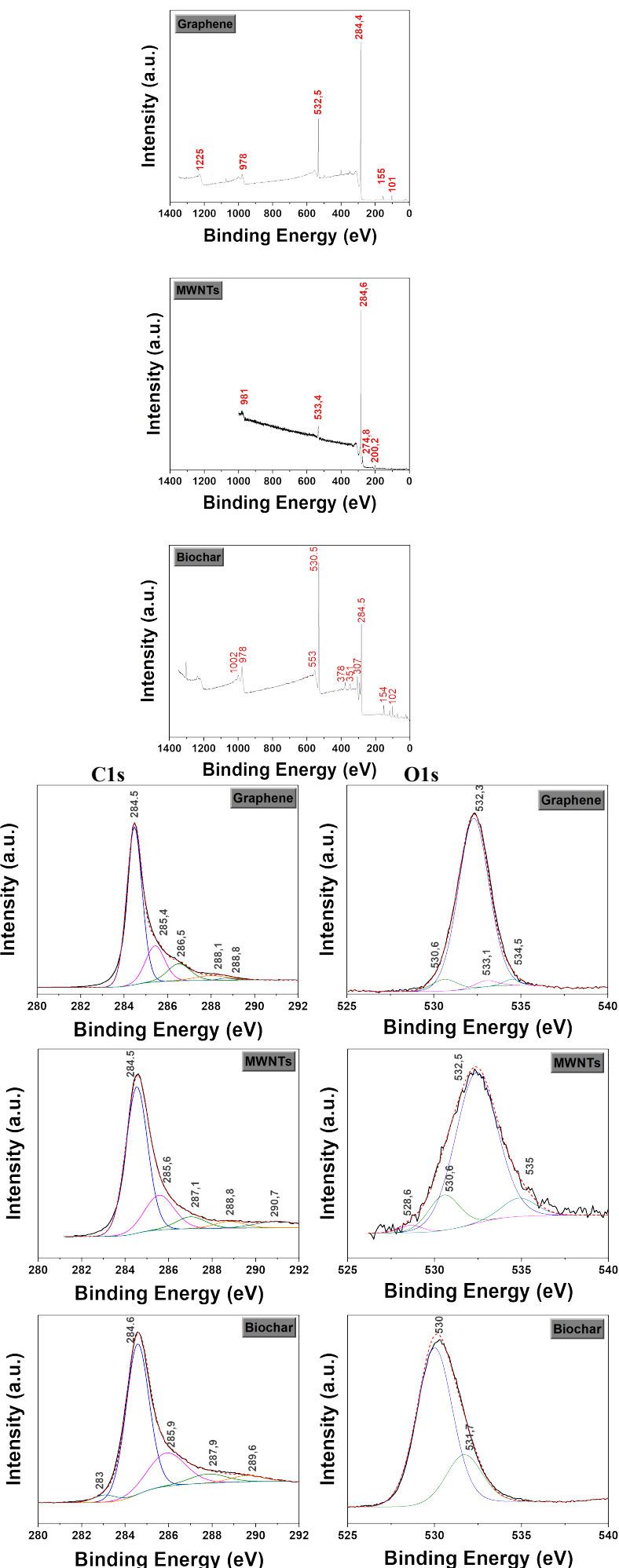


Fig. 7: Expanded XPS survey spectra and their deconvoluted C1s and O1s for graphene, MWNTs and biochar.

Whereas, in the case of biochar, the dominant chemical bond is found around 531 eV corresponding to the O=C or O-C=O bond accompanied just by another weak bond around 532 eV (O-C / C-O-C).

IV. CONCLUSION

According to these results that have been presented in this investigation after comparing physico-chemical properties of three kind of carbonaceous nanomaterial, MWNTs and graphene possess crystalline structures while biochar have amorphous structure with porous texture as proved precisely through their morphological, Raman and XPS spectroscopy. This difference focalizing on the porosity and specific surface area as well as their functional groups concentration and type is a main feature that makes each of them with particular application in various fields, like in: energy storage, environment depollution, biosensing and soil fertilization.

ACKNOWLEDGMENT

The authors also thank the Algerian minister program and Directorate General for Scientific Research and Technological Development (DGRSDT) from Algeria for financial support. We express our gratitude and sincere thanks to Prof. Z. Mekhalif and CES research group (Fundp-Namur University-Belgium) for their help in XRD, XPS and FESEM microscopy. We are also very grateful to Dr J. El- Haskouri (Valencia polytech – Spain) and Prof. D. Begin (ICPEES – Strasbourg-France) for their help in sample characterizations using (TGA and Raman) and (XPS, HRTEM), respectively.

REFERENCES

- [1] A. Nsamirizi, P. Montréal, B. Sinclair-Desagné, “Les Nanotechnologies : leurs bénéfices et leurs risques potentiel”, Série Scientifique CIRANO, pp. 5-43, 2004. <https://www.researchgate.net/publication/5004757>
- [2] V.D. Rajput, T. Minkina, B. Ahmed, V.K. Singh, S. Mandzhieva, S. Sushkova, T. Bauer, K.K. Verma, S. Shan, E.D. van Hullebusch, B. Wang, “Nano-biochar: A novel solution for sustainable agriculture and environmental remediation”, Environmental Research, Vol. 210, pp. 112891, 2022. <https://doi.org/10.1016/j.envres.2022.112891>
- [3] A.B. Duwiefuah, S.J. Cobbina, N. Bakobie, “Review of Eco-Friendly Biochar Used in the Removal of Trace Metals on Aqueous Phases”, International Journal of Environmental Bioremediation & Biodegradation, Vol. 5, No. 2, pp. 27-40, 2017. [DOI:10.12691/ijebb-5-2-1](https://doi.org/10.12691/ijebb-5-2-1)
- [4] S.K. Krishnan, E. Singh, P. Singh, M. Meyyappan, and H.S. Nalwa, “A review on Graphene-based nanocomposites for electrochemical and fluorescent biosensors”, RSC Adv., Vol. 9, pp. 8778–8881, 2019. [DOI: 10.1039/c8ra09577a](https://doi.org/10.1039/c8ra09577a)
- [5] A. Muzaffar, M.B. Ahamed, K. Deshmukh, J. Thirumalai, “A review on recent advances in hybrid supercapacitors: Design, fabrication and applications”, Renewable and Sustainable Energy Reviews, Vol. 101, pp. 123–145, 2019. <https://doi.org/10.1016/j.rser.2018.10.026>
- [6] K. Itami and T. Maekawa, “Molecular Nanocarbon Science: Present and Future”, Nano Lett., Vol. 20, pp. 4718–4720, 2020. <https://dx.doi.org/10.1021/acs.nanolett.0c02143>
- [7] L. Bao1, Y.P. Xie and L. Qie, “Editorial: Nanocarbons: Basics and Advanced Applications”, Front. Chem., Vol. 9, pp. 657941, 2021. [doi: 10.3389/fchem.2021.657941](https://doi.org/10.3389/fchem.2021.657941)
- [8] N. Baig, I. Kammakakam and W. Falath, “Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges”, Mater. Adv., Vol. 2, pp. 1821, 2021. [DOI: 10.1039/d0ma00807a](https://doi.org/10.1039/d0ma00807a)
- [9] S.A. Afolalu, S.B. Soetan, S.O. Ongbali, A.A. Abioye, A.S. Oni, “Morphological characterization and physio-chemical properties of nanoparticle - review”, IOP Conf. Series: Materials Science and Engineering, Vol. 640, pp. 012065, 2019. [doi:10.1088/1757-899X/640/1/012065](https://doi.org/10.1088/1757-899X/640/1/012065)
- [10] O. Guellati, “Synthèse de Nanotubes de Carbone “NTCs” par CVD : Purification et caractérisation”. Thèse de Doctorat, Université Badji-Mokhtar de Annaba, Algérie, 2013.
- [11] O. Guellati et al., “Gas flow and température synthèses dependence on the CNTs structure and yield”, International journal Nanoélectroniques and Materials, Vol. 3, pp.123-131, 2010.
- [12] O. Guellati, D. Bégin, F. Antoni, M. Guerioune, C. Pham-Huu, I. Janowska, “CNTs” array growth using the floating catalyst-CVD method

- over different substrates and varying hydrogen supply". *Materials Science & Engineering B*, vol. 231, pp. 11-17, 2018. <https://doi.org/10.1016/j.mseb.2018.03.001>
- [13] S.L. Pirard, D. Sigrid, J. P. Pirard, "Procédé et installation de fabrication de nanotubes de carbone extrapolables à l'échelle industrielle", *Chimie Nouvelle*, Vol. 119, pp. 1-12, 2015. <http://chimienouvelle.be/CN119web/>.
- [14] I. N. Mazov, N.A. Rudina, A.V. Ishchenko, V. L. Kuznetsov, A. I. Romanenknikee, O.B. Anikeeva, V.I. Suslyayev, V.A. Zhuravlev, "Structural and physical properties of MWNT/polyolefine composites", *Fullerenes Nanotubes and Carbon Nanostructures*, Vol. 20, pp. 510-518, 2012. <https://doi.org/10.1080/1536383X.2012.655956>.
- [15] V. Kumar, A. Kumar, D-J. Lee, S-S. Park, "Estimation of Number of Graphene Layers Using Different Methods: A Focused Review", *Materials*, Vol. 14, pp. 4590, 2021. <https://doi.org/10.3390/ma14164590>.
- [16] F. Abbaci, A. Nait-Merzoug, O. Guellati, A. Harat, J.El Haskouri, J. Delhalle, Z. Mekhalif, M. Guerioune, "Bio/KOH ratio effect on activated biochar and their dye based wastewater depollution", *Journal of Analytical and Applied Pyrolysis*, Vol. 162, pp. 105452, 2022. <https://doi.org/10.1016/j.jaap>.
- [17] Y. Dai, H. Zheng, Z. Jiang, Z. B. Xing, "Combined effects of biochar properties and soil conditions on plant growth: A meta-analysis", *Science of the Total Environment*, Vol. 713, pp.136635, 2020. <https://doi.org/10.1016/j.scitotenv>.
- [18] G. Pilon, "Etude de production et de caractérisation de Biocharbons de panic erige (*panicum virgatum* L.) obtenus par pyrolyse", Thèse de Doctorat, Université de SHERBROOKE, 2013.
- [19] H. Ba, L. Truong-Phuoc, C. Pham-Huu, W. Luo, W. Baaziz, T. Romero, and I. Janowska, "Colloid Approach to the Sustainable Top-Down Synthesis of Layered Materials, *ACS Omega*, Vol. 2, pp. 8610–8617, 2017. DOI: [10.1021/acsomega.7b01311](https://doi.org/10.1021/acsomega.7b01311).
- [20] G. Surekha, K.V. Krishnaiah, N. Ravi, R. Padma Suvama, " FTIR, Raman and XRD analysis of graphene oxide films prepared by modified Hummers method", *J. Phys. Conf. Ser.*, Vol. 1495, pp. 012012 (2020). [doi:10.1088/1742-6596/1495/1/012012](https://doi.org/10.1088/1742-6596/1495/1/012012).
- [21] L.S. Mpeta, S.S. Gwebu, O.A. Arotiba, N.W. Maxakato, "Methanol Oxidation in Alkaline Media with Pt-Au/fMWCNTs and Pt-Pd/fMWCNTs Electrocatalysts on an Exfoliated Graphite Electrode", *Electrocatalysis*, Vol. 10, pp. 672–679, 2019. [doi: 10.1007/s12678-019-00555-0](https://doi.org/10.1007/s12678-019-00555-0)
- [22] O. Guellati, F. Antoni, M. Guerioune, D. Bégin, "New doping process mode to synthesize in situ N-MWNTs in novel coaxial nanostructure", *Catalysis Today*, Vol. 301, pp 164-171, 2018. <https://doi.org/10.1016/j.cattod.2017.03.041>
- [23] A. Sayah, "Elaboration et caractérisation de matériaux composites : polymère organique conducteur modifié par incorporation de Graphene", Thèse de Doctorat, Université Ferhat Abbas de Sétif-1, Algérie, 2018.
- [24] K. Haddad, "Etude de la pyrolyse de matériaux biosourcés chimiquement modifiés : Caractérisation des Biochars et application agronomique", Thèse de Doctorat, Université de HAUTE ALSACE Discipline, Tunisie, 2018.
- [25] R. Al-Gaashani, A. Najjar, Y. Zakaria, S. Mansour, M.A. Atieh, "XPS and structural studies of high quality graphene oxide and reduced graphene oxide prepared by different chemical oxidation methods", *Ceram. Int.*, Vol. 45, pp. 14439–14448, 2019. <https://doi.org/10.1016/j.ceramint.2019.04.165>.



Hanene ARAISSIA Phd in Applied physics, Domain of research : Recycling, **biochar**, Soil treatment.



Ouanassa Guellati, permanent researcher in LEREC laboratory in Algeria and Teacher at Souk-Ahras University, has completed her PhD from Badji-Mokhtar University of Annaba 2013, Algeria on production of Carbon nanotube (CNTs) using CCVD technique and their functionalization and macronisation. She has published 23 papers in reputed journals with high impact factor. She has presented in september 2020 her university habilitation at Badji-Mokhtar University of Annaba. She is current reviewer in *Nanoscale Research Letters* and *Materials Science and Engineering B – Journal Elsevier*. Actually, she is working on the production of smart nanomaterials like transition metal hydroxides, oxides and nanostructured polyaniline and their nanocomposites / nanohybrids with CNTs and/or graphene as well as mesoporous biochar for energy storage, environment and Biosensing application. She is working in collaboration with ICPEES at ECPM, Strasbourg – France, IMS at University of Valencia – Spain, CES at Namur University, SARCHI Chair in Carbon Technology and Materials at Pretoria University, South Africa and DISAT - Politecnico di Torino, Italy.

Goethite Nanofibers /CNTs based Nanocomposites Synthesized by Free-Template Hydrothermal Method and their Physico-Chemical Properties for Energy Storage Application

Sara Djelamda, Fahima Djefaflia, Aicha Harat, Aissa Nait-Merzoug, Damilola Momodu, Ncholu Manyala,

Mohamed Guerioune and Ouanassa Guellati

Abstract—In this investigation, we report the synthesis of Goethite-NFs/CNTs nanocomposites using hydrothermal method at optimized growth condition. These nanostructured products have been characterized in order to identify their physico-chemical properties by different techniques, such as X-Ray Diffraction (XRD), Raman Spectroscopy, High Resolution Scanning Electron Microscopy (FESEM), Thermal analysis (TGA/DTA) and UV- Vis Spectroscopy. The obtained Goethite nanofibers (NFs) have shown structured triangular base nanofibers with diameter in the range [181 - 363 nm]. Using nested and twisted CNTs (MWNTs type) but fairly homogeneous in diameter around 48 nm, the formation of an assembly of two forms (MWNTs and iron oxide Nanofibers) in nanocomposite configuration confirms the significant improvement of their physico-chemical properties, like the increase in their electrical conductivity proven by their obtained gap energy E_g from 3.12 to 2.50 eV. Consequently, the reached results prove clearly that this kind of iron oxide-NFs/MWNTs based nanocomposites can be excellent candidate as electroactive nanomaterials for energy storage application.

Keywords— Nanotechnology, Iron Hydroxide/Oxide, Hydrothermal Process, Optical Properties, Gap Energy.

I. INTRODUCTION

Energy field is one of the most important prospects that have been highlighted in last years. Therefore, the energy storage is considered as nature friend and in order to face the ever-assisted energy crisis, scientists are seeking to find storage devices with high efficiency and low cost production [1, 2].

Additionally, transition metal oxides based on Ni, Mn, Fe or Co, with variable oxidation states are among the incoming materials that have many applications due to their multiple advantages, such as : optical and energy-storage devices, biomedical and biotechnological fields [3-5]. Nowadays, iron oxides/hydroxides are widely and increasingly used in many applications, much more in biomedical, waste water treatment, energy storage and optical devices due to their super-

paramagnetic, safety, low cost synthesis and high electrical conductivity properties [3, 5-8]. More specifically, among them there is hematite (α -Fe₂O₃), maghemite (γ -Fe₂O₃), magnetite (Fe₃O₄), bixbyite (β -Fe₂O₃) and wustite (FeO) as oxides; whereas hydroxides like oxy-hydroxide (Fe(OH)₂, Fe(OH)₃ and mineral goethite (FeOOH)) [9-11]. Hematite is thermodynamically the more stable mineral than others in the presence of oxygen [11, 12] and evinces, strong electron-electron correlations and electron-photon coupling showing interesting optical properties due to their unique complex electronic structures [13]. However, Magnetite (Fe₃O₄) is used in many fields due to their unique nature and it contains both secondary (II) and tertiary iron (III) [14, 15]. For iron based hydroxides case, Goethite (α -FeOOH) is one of the most wide spread minerals in the soil, with an orthorhombic structure illustrating the most stable iron hydroxide. It turns into hematite at 300°C [16-18].

Moreover, Goethite is used with reduced Graphene Oxide to remove lead from wastewater via adsorption technique. The lead ion is considered one of the most dangerous metals, as it affects several systems, such as nervous system, digestive system, kidneys, heart and blood vessels [19]. On the other hand, Biochar-supported Al-Substituted Goethite (BAG) is used also as a new absorbent in order to get rid of polluted nitrates in groundwater [20]. More importantly, Huan Xu and al. found that the specific capacitance of alpha-iron oxy-hydroxide/reduced Graphene oxide (α -FeOOH/rGO) composites is around 452 F.g⁻¹ obtained at a current density 1 A.g⁻¹ [21]. On the other hand, Rasmita Barika found that the specific capacitance is equal to 160 F.g⁻¹ for α -FeOOH [22]. Furthermore, nanocomposites are a combination of massive matrix with nanometric reinforcement with new properties resulting from structural and chemical combination. Thus, in this investigation we report the successful fabrication of Goethite-NFs/CNTs nanocomposites using hydrothermal technique at optimized growth condition. These nanostructured products have been characterized in order to

Manuscript received October 9, 2022; revised July 5, 2023.

S. Djelamda is with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA. (e-mail: saradjelamda1996@gmail.com)

F. Djefaflia, A. Nait-Merzoug and O. Guellati are with Mohamed Chérif Messaadia University, BP. 1553, Souk-Ahras 41000, ALGERIA and LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mails: djefafliafahima@gmail.com, abenlala@yahoo.fr and guellati23@yahoo.fr)

A. Harat and M. Guerioune are with LEREC Laboratory, Physic Department, Badji Mokhtar University of Annaba, BP. 12, Annaba 23000, ALGERIA. (e-mails: harat_aicha@yahoo.fr and mguerioune@yahoo.fr)

D. Momodu and N. Manyala are with Department of Physics, Institute of Applied Materials, SARChI Chair in Carbon Technology and Materials, University of Pretoria, Pretoria 0028, SOUTH AFRICA. (emails: dymomodu@yahoo.com, ncholu.manyala@up.ac.za)

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.159

identify their physico-chemical properties for specific energy application fields. Consequently, oxygen functionalized MWNTs (O-MWNTs) can be a real choice because of their low-cost local production and their lower impact on the environment compared with other materials in different application field. In addition, the local synthesized MWNTs used in this work possess interesting characteristics (structural, textural and chemical) for later application, such as : high purity around 98%, high selectivity, oxygen based functional groups and specific surface area around 150 m²/g.

II. EXPERIMENTAL PROCEDURE

A. Goethite/CNTs synthesis

The experimental protocol implemented during the synthesis of iron oxide based products with and without the presence of CNTs (MWNTs type synthesized in LEREC laboratory [23]) using hydrothermal process goes through the following stages : firstly, we dispersed an iron precursor (FeCl₂.4H₂O) (with or without CNTs) in distilled water under magnetic stirring “250 rpm” for 30 min. Then, a quantity of NaOH was added slowly under stirring for 10 min. Secondly, the resulting orange (or blacked orange in the presence of CNTs) solution was introduced into an 40 mL Teflon-lined hydrothermal autoclave system which has been kept at 120°C in a furnace for 18 h. Lastly, after cooling down naturally to room temperature, the obtained products were always washed, rinsed with distilled water and filtered several times until a neutral pH.

B. Characterization techniques

X-Ray Diffraction (XRD) spectra have been obtained through the X' Pert PRO diffractometer (PANalytical BV, Netherlands) with theta/theta geometry operating from an anti-cathode source Co-K α (λ = 1.79 Å) at 35 kV voltage and 50 mA current in the 2 θ range [5-90°]. Raman spectra of the samples were recorded on a Jobin Yvon Horiba TX 6400 micro-Raman spectrometer excited with 514 nm line of an argon laser with power energy 0.33 mW. The surface morphology of the pure Goethite (Fe₂O₃.H₂O), carbon nanotubes (CNTs) and their nanocomposite (Goethite nanofibers/CNTs) were analyzed by field emission scanning electron microscopy (FESEM) Zeiss Ultra plus 55 at 2 kV accelerating voltage and high resolution transmission electron microscopy (TEM) carried out with a JEOL JEM-2100F microscope operated at 200 kV (Akishima-shi, Japan). Thermal analysis (TGA/DTA) was carried out using a Thermo Gravimetric Analysis instrument (TA Instruments Q600 Simultaneous (DSC/TG) analyzer). The temperature was increased from room temperature to 1000 °C with a heating rate of 10 °C.min⁻¹ under air atmosphere. However, the optical properties were performed by measuring the absorbance using UV-Vis spectrophotometer (Thermo Technical GENESYS 10S) with double beam in order to study the energy band gap of these products.

III. RESULTS AND DISCUSSION

X-ray diffraction is most commonly used as a structural identification tool to characterize and to study the crystalline appearance of the synthesized products using the hydrothermal technique. Figure 1 illustrates the typical XRD patterns of synthesized Goethite nanostructures and their nanocomposite “Goethite/CNTs” using a free template hydrothermal method at optimized conditions. These diffractograms have been identified through their most intense

peaks which are always indexed using a standard (JCPDS) database. They clearly confirm the formation of an hydrated iron oxide phase (Fe₂O₃.H₂O) equivalent of two Goethite (FeOOH) and its nanocomposite with MWNTs known via their characteristic peak at 26.77° corresponding (002) crystalline plan [00-058-1638] [24-26].

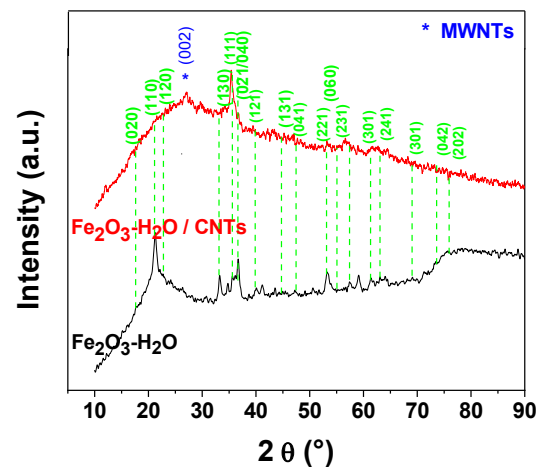


Fig. 1: XRD diffractograms of Goethite and their nanocomposite “Goethite/MWNTs”.

Table. I
CALCULATED CRYSTALLINE PARAMETERS FOR HYDRATED IRON OXIDE (GOETHITE)
SYNTHESIZED BY HYDROTHERMAL METHOD.

PHASE / REF.	a (Å)	b (Å)	c (Å)
Fe ₂ O ₃ .H ₂ O (Goethite)	4.563	10.020	3.016
[00-002-0272]	4.587	9.937	3.015

However, the characteristic peaks of the Goethite type iron oxide phase (Fe₂O₃.H₂O) for these two products are indexed to around 21.46°, 33.17° and 36.65° corresponding to the crystal planes (110), (130) and (111), respectively, which agrees with the previous results [27, 28]. This oxide phase has an orthorhombic structure according to the JCPDS card [00-002-0272]. Moreover, this Goethite phase nanostructure in the nanocomposite case showed a slight shift in the peaks position, which confirms its contact with MWNTs as a second phase.

In addition, the crystalline parameters of this synthesized hydrated iron oxide (Goethite) phase were calculated and shown in table I with values close to those of the JCPDS card [00-002-0272] as an identification reference. On the other hand, the estimated crystallinity degree of pure Goethite is around 23%; whereas it is around 16%, in the case of their nanocomposite with MWNTs.

In the same way, Raman spectroscopy is another technique used to obtain more information about the graphitization and the composition characteristics of the synthesized material. The Raman spectra of these products are illustrated in figure 2. As a result, in the case of the nanocomposite (Goethite/MWNTs), the Raman spectra present the main Raman vibration peaks around 219, 289, 372 and 689 cm⁻¹ corresponding the stretch bond vibrations found in Fe-O, Fe-OH, Fe-O-Fe and Fe-O oxides, respectively [3, 29, 30].

While, D and G band characteristic peaks corresponding the MWNTs formation are found around 1350/1575 cm⁻¹ (Fig. 2a) and 1348/1583cm⁻¹ (Fig. 2b), in pure (MWNTs) and nanocomposite (Goethite/MWNTs), respectively. The G band is a characteristic of the hybridization of carbon atoms

corresponding to tangential vibrations mode of elongation C-C bonds; which is generally a strong indication of the crystallinity/graphitization degree of carbon nanotubes.

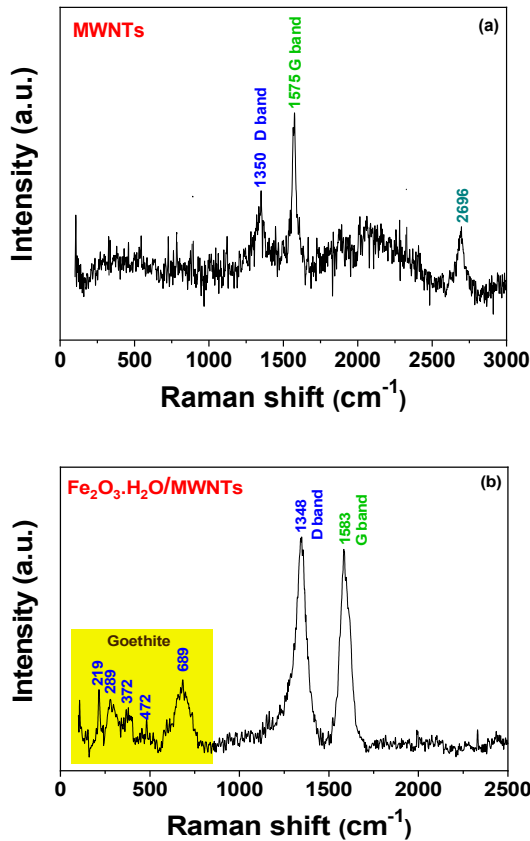


Fig. 2: Raman spectra of pure MWNTs (a) and their nanocomposite (b) (Goethite/MWNTs).

Otherwise, the D band is associated to the disorder in the tubular structure nanotubes where their intensity characterizing the defects concentration. However, the peak found around 2696 cm^{-1} corresponds to the 2D band, as the second order harmonic of the D band, which can be used to differentiate the CNTs properties [31, 32, 33]. These peaks characterizing the used MWNTs are found shifted in the produced nanocomposite due to the incorporation of iron oxide nanostructure and their contact. Table II regroup the MWNTs peaks characteristics with and without Goethite nanostructure.

Table. II

COMPARISON BETWEEN PEAKS POSITIONS AND THEIR RELATIVE INTENSITIES RATIO.

PRODUCT	D (cm^{-1})	G (cm^{-1})	I_D/I_G
MWNTs	1350	1575	0.52
Goethite/MWNTs	1348	1583	1.06

Moreover, we can notice an increase in the I_D/I_G ratio estimating the defect to twice in the nanocomposite (Goethite/MWNTs) case indicating their contact, which proves thereby the decrease found in the crystallinity degree estimated by XRD analysis.

Thermal Characteristics: In order to have idea on the Goethite concentration in the synthesized nanocomposite, we have also performed thermogravimetric analysis (TGA/DTA) under air where we have followed the weight loss evolution in function of oxidation temperature, as represented in figure 3. We can see two main oxidation peaks at 271 and 551 $^{\circ}\text{C}$ indicating the produced nanocomposite selectivity and purity.

The first peak corresponding temperature inferior to 300 $^{\circ}\text{C}$ clearly confirms the Goethite (hydrated iron oxide) transformation into iron oxide; however, 551 $^{\circ}\text{C}$ confirm the functionalized MWNTs combustion [34]. Moreover, this thermal spectra show that this nanocomposite is thermally stable beyond 600 $^{\circ}\text{C}$. From TGA, the first loss around 6 wt.% is attributed to dehydroxylation of Goethite due to their transformation into hematite, as reported previously in the literature [35]. Nevertheless, the second loss around 20 wt.% is attributed to the oxidation of MWNTs by atmospheric oxygen or iron oxide second phase at around 551 $^{\circ}\text{C}$ which is also consistent with work found in Debski's team publication [26].

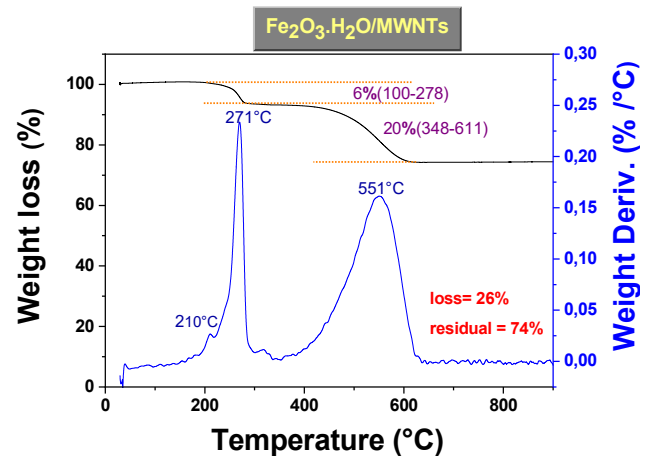


Fig. 3: Thermal analysis (TGA/DTA) of Goethite/MWNTs nanocomposite produced by hydrothermal process.

From these TA analysis curves, we can conclude that this product is composed of around 70 wt.% Goethite (metal oxide) and 30 wt.% MWNTs (carbon).

Morphological properties: From another side, high resolution microscopy analyses have provide precisely more information about the products textural properties by visualizing the products morphology that affect directly the physico-chemical properties. It is clear that through these micrographs at different resolutions, we can observe the formation of nanofibers (NFs) having a triangular structured base of Goethite, as illustrated in figure (4a'). These nanostructured uni-dimensional forms (1D) have diameters around [181-363 nm] [3]. However, figure (4a) represent FESEM micrograph of selective MWNTs which present homogeneous cylindrical shapes as nested and twisted filament with diameter around 48 nm as generally found in the literature [36, 37].

The following figures (4b and 4b') at two different resolutions show the obtained nanocomposite composed of Goethite and MWNTs where we clearly observe the formation of an assembly of two nanostructured forms, carbon nanotubes and Goethite nanofibers which allow the two nanomaterial properties combination basing on carbon with metal transition oxide.

Optical characteristics: Absorption spectra as a function of wavelength in the UV-Vis range [200-1100 nm] for these two products Goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and its nanocomposite (Goethite/MWNTs) synthesized by the hydrothermal method are shown in figure 5. They show a remarkable absorbance with absorption peaks around 290 and 375 nm for Goethite and 274, 363 and 491 nm for its nanocomposite with MWNTs. These peaks illustrate the electronic transitions from valence to conduction band.

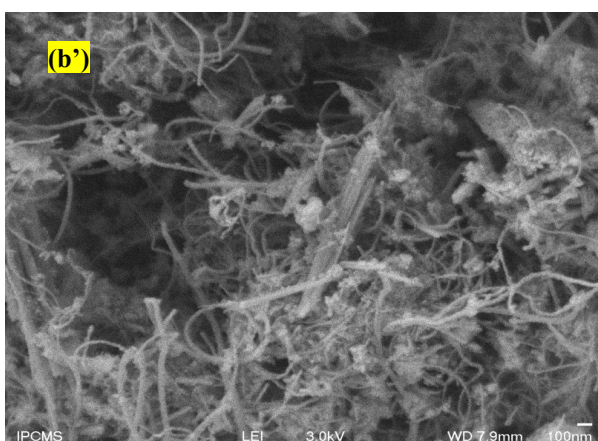
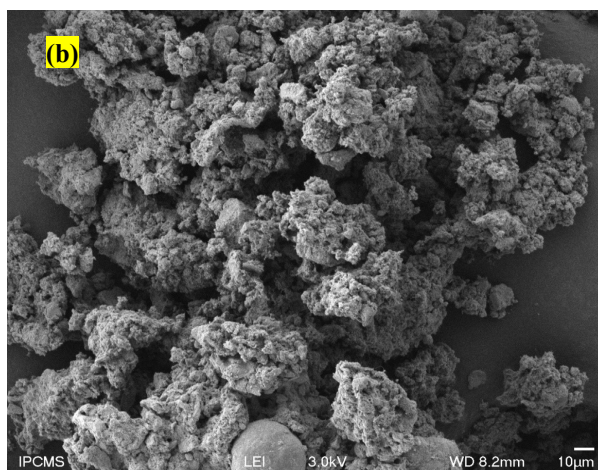
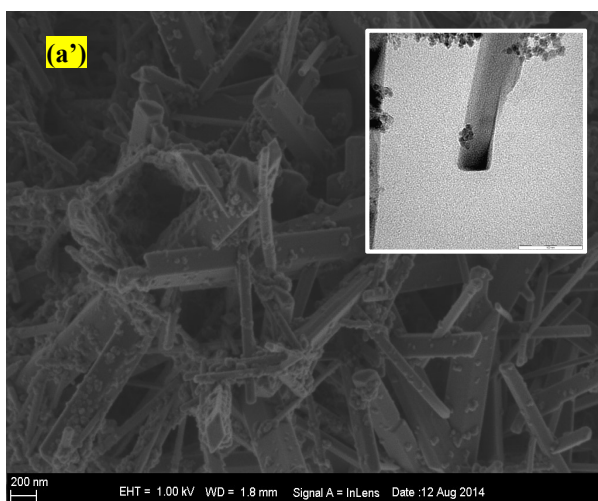
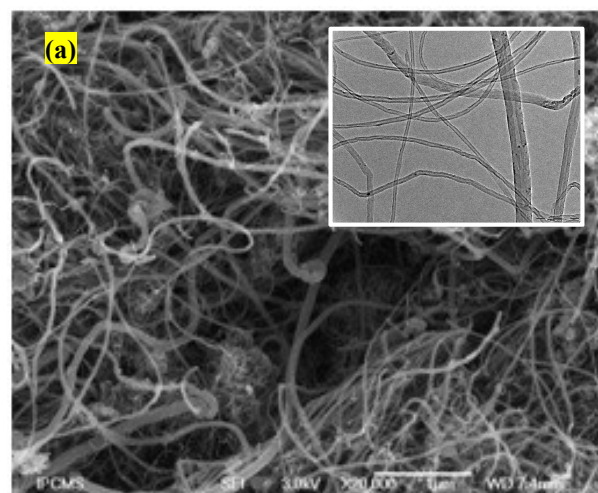


Fig. 4: FESEM micrographs of the obtained MWNTs (a), Goethite based nanofibers (NFs) (a') and their Goethite-NFs/MWNTs nanocomposite (b) and (b') synthesized with hydrothermal process.

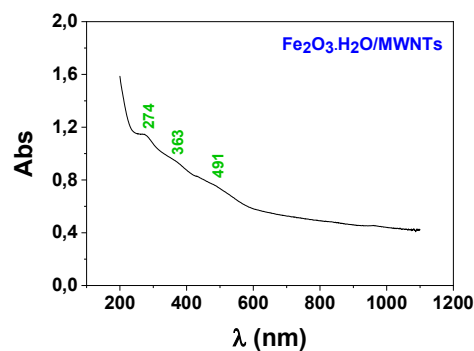
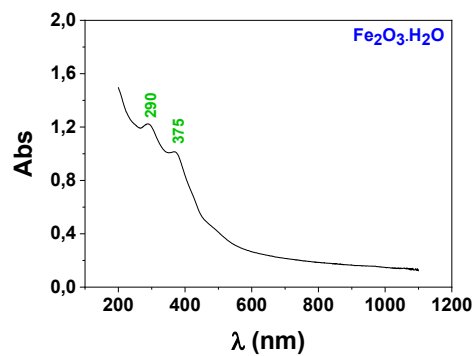


Fig. 5: Absorbance spectra of synthesized Goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and its nanocomposite (Goethite/MWNTs) using hydrothermal process.

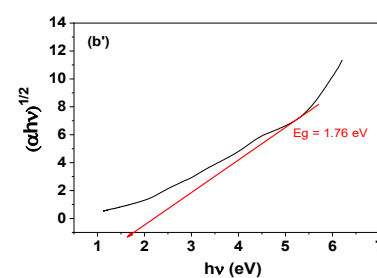
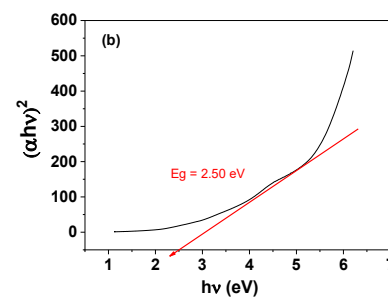
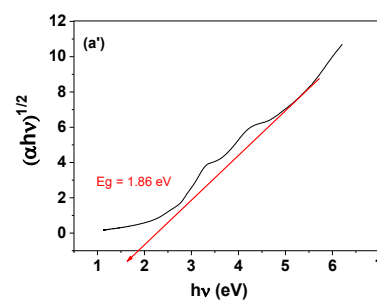
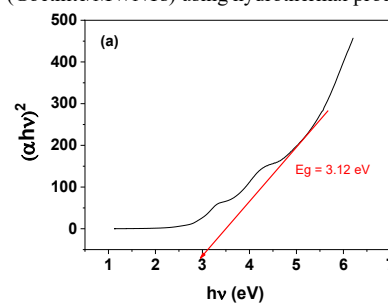


Fig. 6: Gap energy extrapolation for direct and indirect transition in the case of : Goethite (a and a') their nanocomposite Goethite/MWNTs (b and b').

In addition, we have determined the optical gap energy (E_g) using the following Tauc equation which can allow the estimation of the nature and the occurrence of electronic transitions [38]: $(\alpha h\nu)^n = A(h\nu - E_g)$

Where: α is the absorption coefficient; A is a constant; $h\nu$ is the photon energy (eV); E_g is the band gap energy (eV); n is a constant which depends on the type of the electronic transition (n being equal to 2 for direct and 1/2 for indirect transition).

Figure 6 represents the graphic curves of this Tauc equation from the absorption data of these two products in the two suggested cases of electronic transition (direct or indirect transition). Table III regroup their deduced E_g gap energies for these two cases from these Tauc curves using Origin software (via an extrapolation).

Table. III

DEDUCED GAP ENERGY (E_g) FROM TAUC CURVES FOR TWO CASES DIRECT AND INDIRECT ELECTRONIC TRANSITION.

ELECTRONIC TRANSITION	E_g (eV)	
	Goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)	Goethite/MWNTs
DIRECTE	3.12	2.50
INDIRECTE	1.86	1.76

These results clearly indicate that these products are semiconductors with $E_g < 4$ eV. On the other hand the nanocomposite based on Goethite/MWNTs (70:30 wt.% estimated from TGA analysis) should have a higher electrical conductivity than pure Goethite according to its lower deduced E_g in comparison to Goethite values; this is in agreement with reported results found in the literature [39].

IV. CONCLUSION

In this work, we have studied the experimental results obtained through the synthesis of Goethite hydrated iron oxide and their nanocomposite (Goethite/MWNTs) using hydrothermal process under optimized condition. We identified these products from structural and morphological aspect point of view as well as their thermal and optical properties.

Moreover, these products have shown the formation of Goethite based nanostructured fibers (NFs) with triangular base and carbon-based nanotubes (CNTs) with diameters around 200 nm and 48 nm, respectively, with good dispersion and selectivity.

According to the obtained results, it is confirmed that the addition of MWNTs to iron oxide (Goethite type) significantly improves their physic-chemical properties such as the increase in their electrical conductivity proven by the deduced gap energy E_g from their absorption of UV-visible light, which is lower in comparison to that of pure iron oxide. On the other hand, there is a degradation in crystallinity/graphitization degree and an increase in the defects as indicated by XRD and Raman spectroscopy analysis, respectively, proved for the last through the I_D/I_G intensities ratio and the displacement of peaks position.

ACKNOWLEDGMENT

We express our gratitude and sincere thanks to Prof. N. Manyala (SARChI) team, Prof. D. Begin (ICPEES) and Prof. F. Antoni (ICub) for their help in FESEM and Raman analysis systems. The authors also thank the Algerian minister program and Directorate General for Scientific Research and

Technological Development (DGRSDT) from Algeria for financial support.

REFERENCES

- [1] J. Yang, Y. Liu, S. Liu, L. Li, C. Zhang and T. Liu, "Conducting polymer composites: Material synthesis and applications in electrochemical capacitive energy storage", *Journal of Materials Chemistry Frontiers*, Vol. 1(2), pp. 251–268, 2017. <https://doi.org/10.1039/c6qm00150e>
- [2] M.M. Rahman, P.M. Joy, M.N. Uddin, M.Z. Bin Mukhlis and M.M.R. Khan, "Improvement of capacitive performance of polyaniline based hybrid supercapacitor", *Journal of Heliyon*, Vol. 7(7), pp. e07407, 2021. <https://doi.org/10.1016/j.heliyon.2021.e07407>
- [3] M. Boufas, O. Guellati, A. Harat, D. Momodu, J. Dangbegnon, N. Manyala and M. Guerioune, "Optical and electrochemical properties of iron oxide and hydroxide nanofibers synthesized using new template-free hydrothermal method", *Journal of Nanostructure in Chemistry*, Vol. 10(4), pp. 275–288, 2020. <https://doi.org/10.1007/s40097-020-00348-8>
- [4] M. Manjunatha, R. Kumar, A.V. Anupama, V.B. Khopkar, R. Damle, K.P. Ramesh and B. Sahoo, "XRD, internal field-NMR and Mössbauer spectroscopy study of composition, structure and magnetic properties of iron oxide phases in iron ores", *Journal of Materials Research and Technology*, Vol. 8(2), pp. 2192–2200, 2019. <https://doi.org/10.1016/j.jmrt.2019.01.022>
- [5] A.B. Sengul and E. Asmatulu, "Toxicity of metal and metal oxide nanoparticles", *Journal of Environmental Chemistry Letters*, vol. 18(5), pp. 1659–1683, 2020. <https://doi.org/10.1007/s10311-020-01033-6>
- [6] Q. Feng, Y. Liu, J. Huang, K. Chen, J. Huang and K. Xiao, "Uptake, distribution, clearance, and toxicity of iron oxide nanoparticles with different sizes and coatings", *Journal of Scientific Reports*, Vol. 8(1), pp. 1–13, 2018. <https://doi.org/10.1038/s41598-018-19628-z>
- [7] P. Tartaj, M.P. Morales, T. Gonzalez-Carreño, S. Veintemillas-Verdaguer and C. J. Serna, "The iron oxides strike back: From biomedical applications to energy storage devices and photoelectrochemical water splitting", *Journal of Advanced Materials*, Vol. 23(44), pp. 5243–5249, 2011. <https://doi.org/10.1002/adma.201101368>
- [8] P. Xu, G.M. Zeng, D.L. Huang, C.L. Feng, S. Hu, M.H. Zhao, C. Lai, Z. Wei, C. Huang, G.X. Xie and Z.F. Liu, "Use of iron oxide nanomaterials in wastewater treatment", *Journal of Science of the Total Environment*, Vol. 424, pp. 1–10, 2012. <https://doi.org/10.1016/j.scitotenv.2012.02.023>
- [9] M. Khalid, "Processing and characterization of tailor-made superparamagnetic iron oxide nanoparticles (SPIO-NPs) for pharmaceutical applications", University of Magdeburg Thesis, 2018. <https://141.48.10.209/handle/1981185920/13516>
- [10] Q. Hu, D.Y. Kim, W. Yang, L. Yang, Y. Meng, L. Zhang and H.K. Mao, "FeO₂ and FeOOH under deep lower-mantle conditions and Earth's oxygen-hydrogen cycles treatment", *Journal of Nature*, Vol. 534(7606), pp. 241–244, 2016. <https://doi.org/10.1038/nature18018>
- [11] K. B. Narayanan and S. S. Han, "One-Pot Green Synthesis of Hematite (α -Fe₂O₃) Nanoparticles by Ultrasonic Irradiation and Their In Vitro Cytotoxicity on Human Keratinocytes CRL-2310", *Journal of Cluster Science*, Vol. 27(5), pp. 1763–1775, 2016. <https://doi.org/10.1007/s10876-016-1040-9>
- [12] M. F. Al-Hakkani, G. A. Gouda and S. H. A. Hassan, "A review of green methods for phyto-fabrication of hematite (α -Fe₂O₃) nanoparticles and their characterization, properties, and applications", *Journal of Heliyon*, Vol. 7(1), pp. e0580, 2021. <https://doi.org/10.1016/j.heliyon.2020.e05806>
- [13] Y. H. Chen and C. C. Lin, "Effect of nano-hematite morphology on photocatalytic activity", *Journal of Physics and Chemistry of Minerals*, Vol. 41(10), pp. 727–736, 2014. <https://doi.org/10.1007/s00269-014-0686-9>
- [14] R. A. Revia and M. Zhang, "Magnetite nanoparticles for cancer diagnosis, treatment, and treatment monitoring: Recent advances", *Journal of Materials Today*, Vol. 19(3), pp. 157–168, 2016. <https://doi.org/10.1016/j.matod.2015.08.022>
- [15] U. S. Khan, A. Manan, A. Manan, N. Khan, A. Mahmood, and A. Rahim, "Transformation mechanism of magnetite nanoparticles", *Journal of Materials Science- Poland*, Vol. 33(2), pp. 278–28, 2015. <https://doi.org/10.1515/msp-2015-0037>
- [16] A.T. Jacobson and M. Fan, "Evaluation of natural goethite on the removal of arsenate and selenite from water", *Journal of Environmental Sciences (China)*, Vol. 76, pp. 133–141, 2019. <https://doi.org/10.1016/j.jes.2018.04.016>
- [17] H. Liu, T. Chen, X. Zou, C. Qing and R. L. Frost, "Thermal treatment of natural goethite: Thermal transformation and physical properties", *Journal of Thermochimica Acta*, Vol. 568, pp. 115–121, 2013. <https://doi.org/10.1016/j.tca.2013.06.027>
- [18] H. Liu, T. Chen and R. L. Frost, "An overview of the role of goethite surfaces in the environment", *Journal of Chemosphere*, Vol. 103, pp. 1–11, 2014. <https://doi.org/10.1016/j.chemosphere.2013.11.065>

- [19] F. Gordon-Núñez, K. Vaca-Escobar, M. García, L. Fernández, A. Debut, M. Sandoval, P. Espinoza-Montero, "Applicability of Goethite/Reduced Graphene Oxide Nanocomposites to Remove Lead from Wastewater", *Journal of nanomaterials*, Vol. 9(11), pp. 1580, 2019. <https://doi.org/10.3390/nano9111580>
- [20] L. Wang, S. Liu, W. Xuan, S. Li, A. Wei, "Efficient Nitrate Adsorption from Groundwater by Biochar-Supported Al-Substituted Goethite", *Journal of sustainability*, Vol. 14, pp.7824, 2022. <https://doi.org/10.3390/su14137824>
- [21] H. Xu, Z. Hu, A. Lu, Y. Hu, L. Li, Y. Yang, Z. Zhang and H. Wu, "Synthesis and super capacitance of goethite/reduced graphene oxide for supercapacitors", *Journal of Materials Chemistry and Physics*, Vol. 141(1), pp. 310–317, 2013. <https://doi.org/10.1016/j.matchemphys.2013.04.048>
- [22] R. Barika, B.K. Jena, A. Dasha, M. Mohapatra, "In-situ synthesis of flowery shape α -FeOOH/Fe₂O₃ nano particles and their phase dependant supercapacitive behaviour", *Journal of The Royal Society of Chemistry*; vol. 1, pp.1–9, 2014. <https://doi.org/10.1039/x0xx00000x>
- [23] O. Guellati, S. Detriche, M. Guerioune, Z. Mekhalif and J. Delhalle, "Gas Flow and Temperature Synthesis Dependence on the CNTs structure and yield", *International Journal of Nanoelectronics and Materials*, Vol. 3 (2), p. 125–134, 2010. E ISBN: 2232-1535
- [24] Ö. Güler, "Mechanical and thermal properties of a Cu-CNT composite with carbon nanotubes synthesized by CVD process", *Journal of Materials Testing*, Vol. 56(9), pp. 662–666, 2014. <https://doi.org/10.3139/120.110615>
- [25] R. Das, S. Hamid, M. Ali, S. Ramakrishna and W. Yongzhi, "Carbon Nanotubes Characterization by X-ray Powder Diffraction – A Review", *Journal of Current Nanoscience*, Vol. 11(1), pp. 23–35, 2014. <https://doi.org/10.2174/1573413710666140818210043>
- [26] N. Debski, "Fibres obtenues a partir de nanotubes de carbone verticalement alignes : élaboration et propriétés", University of South Paris, 2014.
- [27] M. K. Ghosh, G. E. J. Poinern, T. B. Issa and P. Singh, "Arsenic adsorption on goethite nanoparticles produced through hydrazine sulfate assisted synthesis method", *Journal of Chemical Engineering*, Vol. 29(1), pp. 95–102, 2012. <https://doi.org/10.1007/s11814-011-0137-y>
- [28] H. Gupta, R. Kumar, H. S. Park and B. H. Jeon, "Photocatalytic efficiency of iron oxide nanoparticles for the degradation of priority pollutant anthracene", *Journal of Geosystem Engineering*, Vol. 20(1), pp.21–27, 2017. <https://doi.org/10.1080/12269328.2016.1218302>
- [29] K. Hedenstedt, J. Backstr, E. Ahlberg, "In-situ Raman spectroscopy of α - and γ -FeOOH during cathodic load", *J. Electrochem. Soc.*, Vol. 164(9), pp. H621–H627, 2017. K. Hedenstedt, J. Backstr, E. Ahlberg, "In-situ Raman spectroscopy of α - and γ -FeOOH during cathodic load", *J. Electrochem. Soc.*, Vol. 164(9), pp. H621–H627, 2017. DOI:10.1149/2.0731709jes
- [30] M. A. Legodi and D. de Waal, "The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste", *Journal of Dyes and Pigments*, Vol. 74(1), pp.161–168, 2007. <https://doi.org/10.1016/j.dyepig.2006.01.038>
- [31] S. Costa, E. Borowiak-Palen, M. Kruszyńska, A. Bachmatiuk and R.J. Kalenczuk, "Characterization of carbon nanotubes by Raman spectroscopy", *Journal of Materials Science- Poland*, vol. 26(2), pp.433–441, 2008.
- [32] A. Jorio and R. Saito, "Raman spectroscopy for carbon nanotube applications", *Journal of Applied Physics*, Vol. 129(2), 2021. <https://doi.org/10.1063/5.0030809>
- [33] R. G. Abaszade, O. A. Kapush and A. M. Nabiev, "Properties of carbon nanotubes doped with gadolinium", *Journal of Optoelectronic and Biomedical Materials*, Vol. 12(3), pp.61–65, 2020.
- [34] O. Guellati, D. Bégin, F. Antoni, S. Moldovan, M. Guerioune, C. Pham-Huu, I. Janowska, "CNTs' array growth using the floating catalyst-CVD method over different substrates and varying hydrogen supply", *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* Vol. 231, pp. 11–17, 2018. <https://doi.org/10.1016/j.mseb.2018.03.001>
- [35] V.P. Ponomar, "Thermomagnetic properties of the goethite transformation during high-temperature treatment", *Journal of Materials Minerals Engineering*, Vol. 127 (August), pp. 143–152, 2018. <https://doi.org/10.1016/j.mineng.2018.08.016>
- [36] S. Lagoutte, P. H. Aubert, M. Pinault, F. Tran-Van, M. Mayne-L'Hermite and C. Chevrot, "Poly(3-methylthiophene)/vertically aligned multi-walled carbon nanotubes: Electrochemical synthesis, characterizations and electrochemical storage properties in ionic liquids", *Journal of Electrochimica Acta*, Vol. 130, pp. 754–765, 2014. <https://doi.org/10.1016/j.electacta.2014.03.097>
- [37] C. Castro, M. Pinault, D. Porterat, C. Reynaud, and M. Mayne-L'Hermite, "The role of hydrogen in the aerosol-assisted chemical vapor deposition process in producing thin and densely packed vertically aligned carbon nanotubes", *Journal of Carbon*, Vol. 61, pp. 585–594, 2013. <https://doi.org/10.1016/j.carbon.2013.05.040>
- [38] A. Lassoued, B. Dkhil, A. Gadri and S. Ammar, "Control of the shape and size of iron oxide (α -Fe₂O₃) nanoparticles synthesized through the chemical precipitation method", *Journal of Results in Physics*, Vol.7, pp.3007–3015, 2017. <https://doi.org/10.1016/j.rinp.2017.07.066>
- [39] C. Bao, X. Liu, X. Shao, X. Ren, Y. Zhang, X. Sun, D. Fan, Q. We and H. Ju, "Cardiac troponin I photoelectrochemical sensor: {Mo368} as electrode donor for Bi2S3 and Au co-sensitized FeOOH composite", *Journal of Biosensors and Bioelectronics*, Vol.157(March), pp.112–157, 2020. <https://doi.org/10.1016/j.bios.2020.112157>

Sara DJELAMDA Phd in Applied physics, Domain of research: Nanocomposite, Polyaniline, In-situ growth, energy storage.



Ouanassa Guellati, permanent researcher in LEREC laboratory in Algeria and Teacher at Souk-Ahras University, has completed her PhD from Badji-Mokhtar University of Annaba 2013, Algeria on production of Carbon nanotube (CNTs) using CCVD technique and their functionalization and macronisation. She has published 23 papers in reputed journals with high impact factor. She has presented in september 2020 her university habilitation at Badji-Mokhtar University of Annaba. She is current reviewer in Nanoscale Research Letters and Materials Science and Engineering B – Journal Elsevier. Actually, she is working on the production of smart nanomaterials like transition metal hydroxides, oxides and nanostructured polyaniline and their nanocomposites / nanohybrids with CNTs and/or Graphene as well as mesoporous Biochars for energy storage, environment and Biosensing application. She is working in collaboration with ICPEES at ECPM, Strasbourg – France, IMS at University of Valencia – Spain, CES at Namur University, SARChI Chair in Carbon Technology and Materials at Pretoria University, South Africa and DISAT - Politecnico di Torino, Italy.

Optoelectronic and Thermoelectric Properties of the Tetragonal Structure of the Halide Perovskite Material RbSeBr₃ used for low-cost Photovoltaic

Rabah Mehyaoui and Karima Benyahia

Abstract– Perovskite solar cells are the future of energy production due to the high- efficiency and low production costs. In this work, the structural, electronic and optical properties of the tetragonal inorganic halideperovskiteRbSeBr₃ are performed using the full potential linearized augmented plane waves (FP-LAPW) method with the PerdewBurke–Ernzerh generalized gradient approximation (PBE-GGA) as well as the local density approximation (LDA) and the modified Becke–Johnson (mBJ-LDA) as exchange correlation potentials using Wien2k code. Furthermore, the thermoelectric properties have been calculated using BoltzTrap code, the obtained results show that the studied compound (RbSeBr₃) has a metallic character and can be used as an absorber in UV-interval; on the other hand the thermoelectric power reveals a high value.

Keywords: Electronic and Optical properties, Inorganic halideperovskite, Tetragonal RbSeBr₃,FP-LAPW,PBE-GGA,LDA,mBJ-LDA,Wien2k,Thermoelectric properties, BoltzTrap.

NOMENCLATURE

FPLAPW	Full potential Linearized augmented plane wave
PBE-GGA	Perdew–Burke–Ernzerh generalized gradient approximation.
LDA	Local density approximation.
mBJ-LDA	Modified Becke–Johnson LDA.

I. INTRODUCTION

Solar energy is one of the most accessible, cost-effective, and environmentally friendly sources of energy in the world, yet in most locations, the costs associated with harvesting solar energy using traditional photovoltaic's (PVs) are still expensive compared to conventional fossil-fuel energy sources [1,2].

Therefore, it is essential to create next-generation PVs that are both affordable and efficient. Perovskite solar cells (PSCs), a novel thinfilm PVs technology, have just come to attract more attention and research [3, 4]. The power conversion efficiency (PCE) according to Kojima et al. has quickly increased from 3.8% in a short amount of time in 2009 to a verified 22.1% in 2017 [5-6].

The term perovskite originally refers to the mineral calcium titanate with the chemical formula CaTiO₃ [7], which has a very important structure, it is the basis of the definition of a Perovskite [8]; this mineral specie was discovered in Russia by the German G. Rose in 1839. The first studies on perovskites have been concentrated on titanate compounds' structure and biaxial optical characteristics [7]. The ideal

perovskite structure has a cubic unit cell and the general formula ABX₃. The A cation, B cation, and X anion are all positioned in the body's center, the structure is symmetrical in the Oh direction. The perovskite structure was described by V. Goldschmidt in 1926 [9] who studied a large number of synthetic perovskite compounds with different compositions. These compounds were initially employed as pigments in paints and other coatings, in addition to their importance in fundamental research [10]. Electronic properties of perovskites aroused more interest from the mid-1940s, when the ferroelectricity in BaTiO₃ perovskite has been demonstrated [11, 12].

The perovskite RbSeBr₃ crystallizes in the tetragonal P4mm space group. Rb is bound to twelve Br atoms to create RbBr₁₂ cuboctahedra, which share corners with corresponding RbBr₁₂ cuboctahedra of twelve, faces [13]. In this study, we have simply taken into account the tetragonal structure of RbSeBr₃ utilizing PBE-GGA to study its unexplored structural, electronic, optical, and thermoelectric properties. The paper is organized as follows: Part.1 supplies an introduction, Part 2 includes computational details, Part 3 covers the results and we finish with a conclusion

II. COMPUTATIONAL METHODOLOGIES

All calculations in this study were completed using the WIEN2K code's and the implementation of the full-potential linear augmented plane wave (FP-LAPW) method within the confines of density functional theory (DFT) [14,15]. In order to evaluate the prior properties, Perdew-Burke-Ernzerh generalized gradient approximation (PBE-GGA) was used for the calculations [16] as well as the local density approximation (LDA) [17] and modified Becke-Johnson (mBJ-LDA) [18]. A linear combination of the radial Schrödinger equation solution times the spherical harmonic is used in the interstitial region, along with the plane wave basis set. For the tetragonal structure (P4mm space group) the RMT value is 2.5 a.u for the atoms Rb: [Kr] 5s1, Se:[Ar] 3d104s24p4 and Br:[Ar] 3d104s24p5. To expand the wave functions in the interstitial region, we took the value of Kmax =10000. The R_{mt} * K_{MAX} is taken equal to 7 (where k_{max} is the plane waves cutoff) [19]. In the muffintin spheres, the angular momentum expansion is taken into account up to

Manuscript received October 25, 2022; revised July 7, 2023.

R. Mehyaoui and K. Benyahia are with Materials Science and Applications Laboratory (LSMA), BelhadjBouchaib University, AinTémouchent, ALGERIA. (E-mails: rabah.mehyaoui@univ-temouchent.edu.dz, karima.benyahia@univ-temouchent.edu.dz).

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.172

$l_{\max} = 10$. All computations are carried out in a k-mesh with $21 \times 21 \times 21$ k points in the irreducible Brillouin zone.

III. RESULTS AND DISCUSSIONS

1. GEOMETRICAL STRUCTURE AND ITS PROPERTIES

As previously stated, the RbSeBr₃'s tetragonal structure, which is seen in Fig. 1, has been taken into account and optimized. The structure belongs to the P4mm space group [20].

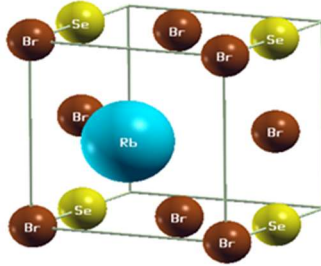


Fig. 1. Tetragonal Structure of RbSeBr₃

To plot the evolution of the total energy as a function of the volume, we used the Murnaghan Equations [21]:

$$E(V) = E_0 + \frac{B_0}{B'(B' - 1)} \left[V \left(\frac{V_0}{V} \right)^{B'} - V_0 \right] + \frac{B_0}{B'} (V - V_0)$$

$$B_0 = V \frac{\partial^2 E}{\partial V^2}$$

$$V = V_0 \left(1 + \frac{B' P}{B_0} \right)^{-1/B'}$$

Where, V_0 is the reference volume, V is the warped volume, B_0 is the bulk modulus, and B' is its derivative. E_0 is the reached minimum ground state energy [21].

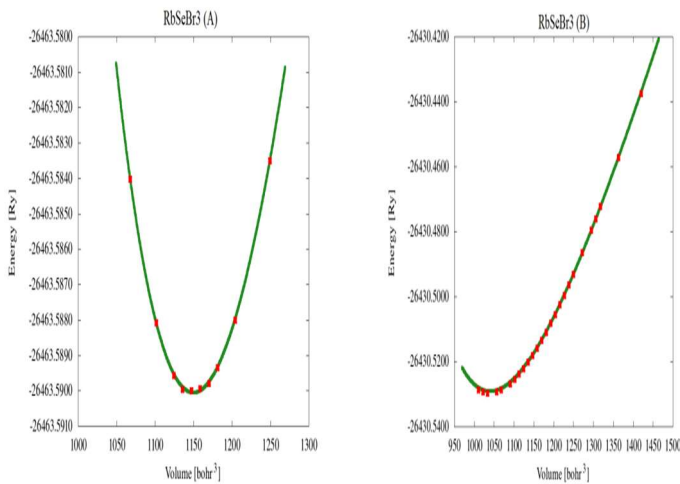


Fig. 2. The variation of the total energy of the tetragonal structure of RbSeBr₃ for: A) GGA B) LDA approximations depending on the volume

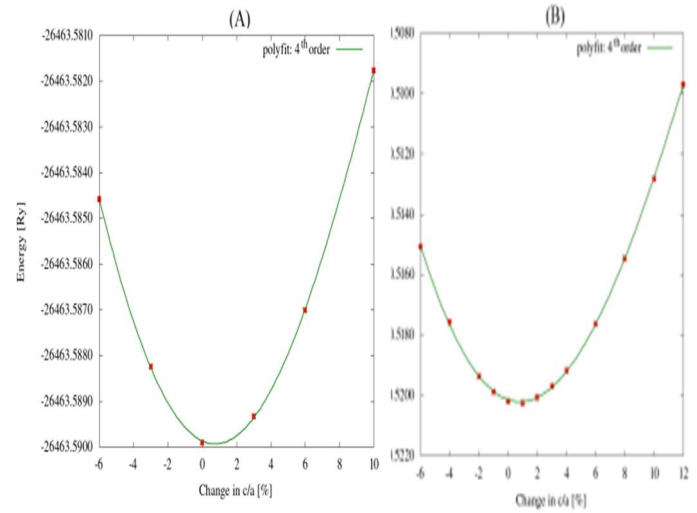


Fig. 3. The variation of C/A ratio of the tetragonal structure of RbSeBr₃ for: A) GGA, B) LDA Approximations with constant volume.

The compounds' ground state minimum energy and optimal volumes are determined from the Figures (2-3). Table I includes the equilibrium parameters, bulk modulus and its derivative, volume, gap energy, and total energies. They agree well with other theoretical calculations [20].

2. ELECTRONIC PROPERTIES

2.1 THE ELECTRONIC BAND STRUCTURE

The band structures for spin-up and spin-down shown in Fig. 4 are computed using the GGA-PBE exchange correlation functionals in order to explore the electronic properties. For this purpose, the high symmetry path of the k-points inside the Brillouin zone taken into account is $\Gamma \rightarrow X \rightarrow M \rightarrow \Gamma \rightarrow Z \rightarrow R \rightarrow A \rightarrow Z \rightarrow X \rightarrow R \rightarrow M \rightarrow A$. From the band structures, the absence of a forbidden band indicates the metallic character of the studied material. The A point contains both the valence band maximum (VBM) and the conduction band minimum (CBM).

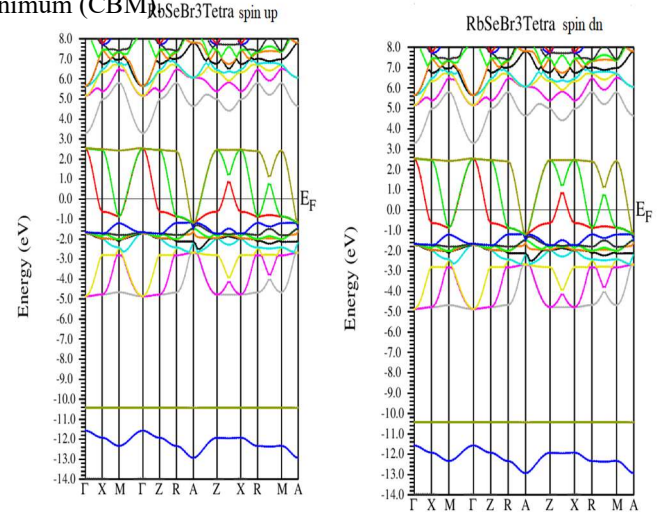


Fig. 4. Band structure of RbSeBr₃ for GGA-PBE Approximation.

Table. I

Lattice parameters (A_0), Bulk modulus B_0 (GPa) and its derivative B' , Total energy (Ry), Fermi energy (Ry) and GAP energy (eV) of the tetragonal structure of $RbSnBr_3$ using GGA, LDA and mBJ -LDA approximations.

Tetragonal structure		a(A°)	b(A°)	c(A°)	$V_0(a-u)^3$	B_0 (GPa)	B'	E(Ry)	E_F (Ry)	E_g (eV)
Murnaghan	GGA	5.458	5.458	5.696	1150.115	26.134	4.587	26463.590	0.0545	0
	LDA	5.364	5.359	5.226	1040.719	37.580	5.953	26430.529	0.2245	0
mBJ -LDA		/	/	/	/	/	/	/	0.2649	0
Other work [20]		5.523	5.523	5.518	1135.853	/	/	/	/	0

Table. II

SPIN MAGNETIC MOMENTS OF MIXED CHARGE DENSITY

INTERSTITIAL	
Rb	0.00037
Se	0.00033
Br(1a)	0.00367
Br(2c)	-0.00177
CELL	-0.00024
	0.00060

2.2 THE DENSITY OF STATES

To gain insight into how the various atoms and their orbitals contribute to the curves in band structures, we estimated the total density of states (TDOS) and partial density of states (PDOS) for the tetragonal structure of $RbSeBr_3$. The TDOS plots shown in Fig. 5 reveal a strong contribution of p-state of the atoms (Se, Br) along the borders of the Fermi level for both spins Up/Dn. The valence band (VB) is dominated by the p-state of the atoms (Se, Br), while the conduction band is characterized by a high contribution of Rb-d states. We notice a low contribution of s states in both bands and the Fermi level is characterized by a high hybridization of Se-p states and Br-p states leading to a metallic character of $RbSeBr_3$ in the tetragonal structure.

3. OPTICAL PROPERTIES

In this work, we examined the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ components of the dielectric constant given by Eq.4 in the energy range(0 – 14)eV. Both components are shown in Fig. 6. the extinction coefficient $k(\omega)$, the electron energy loss spectra (EELS) $L(\omega)$, the reflectivity $R(\omega)$, the optical conductivity $\sigma(\omega)$, the absorption coefficient $\alpha(\omega)$, and the refractive index $n(\omega)$ are displayed in Figures (7,8). These properties, which depend on frequencies and are derived from the complex dielectric function, stated in Eq.4, they are in fact frequency-dependent [23–24].

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) \quad (4)$$

$$n(\omega) = \left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} + \varepsilon_1(\omega) \right)^{1/2} \quad (5)$$

$$k(\omega) = \left(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega) \right)^{1/2} \quad (6)$$

$$R(E) = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (7)$$

$$L(\omega) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} \quad (8)$$

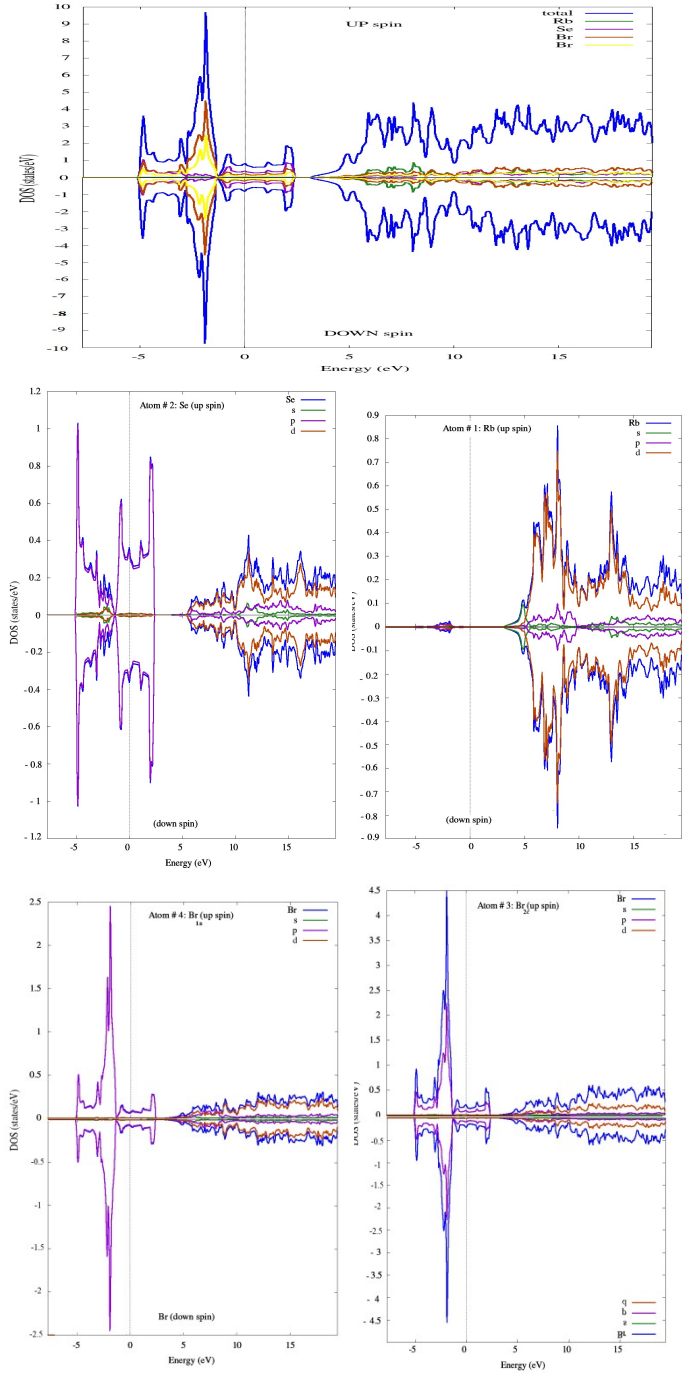


Fig. 5. Total and partial density of state for the tetragonal $RbSeBr_3$

All of the previous properties actually depend only on the components of the dielectric function at specific frequencies which is used to determine the optical properties [25, 26]. The equations Eq. 5–8 are used to obtain their expressions. [24].

Both the electronic polarizability properties of perovskite and the scattering behavior of electromagnetic (EM) radiation incident on perovskite are explained by the curve of the real component of the dielectric function in Fig. 6 related to perovskite photon energy compound [27]. At zero energy of $\epsilon_1(0)$, the static permittivity is -2200 along yy and -350 along xx and zz. It is clear that the value of $\epsilon_1(\omega)$ varies from visible to UV zone (1.7 to 12 eV). Increasing and tending to zero suggest that it behaves like a metal in this region. Inside a metallic conductor, there is no electric field because the free charge remains on the surface of the metal, and a significant plasmonic excitation exists and can survive.

The response of a connection to (EM) radiation is given by the imaginary part of the dielectric function, as shown. 6. This indicates the state transition that occurs from the valence band to the conduction band [27, 28]. We find that $\epsilon_2(0)$ is equal to 16050 along yy and 7000 along xx and zz. After that, this value starts to decrease and approaches zero.

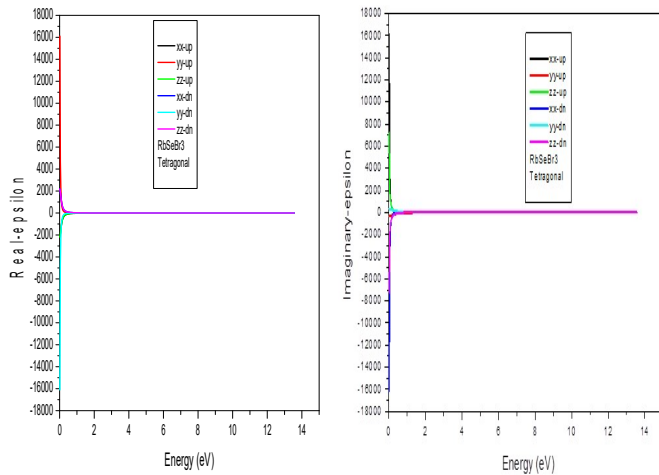


Fig.6. Real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ components of dielectric constant of RbSeBr3.

Figure 7(A) shows the absorption coefficient $\alpha(\omega)$ of RbSeBr3 perovskite, showing how the incident light is absorbed. It also provides information on the degradation of the outgoing light as it passes through the material, showing how EM radiation is attenuated [24, 27]. The value of $\alpha(\omega)$ approaches zero in the range 0 to 1.5 eV. The halide perovskite is nearly optically transparent in these regions because no light absorption occurs. As a result, this compound has negligible absorption in this range. Absorption at (2.8, 7.8, and 11 eV) demonstrates the effectiveness of this material in the UV range. This result demonstrates that RbSeBr3 can be incorporated into sensitive devices as a UV absorber to effectively protect against harmful UV radiation. In contrast, fig. 7 (B) displays the plot of real and imaginary optical conductivity that almost matches the absorption spectra $\alpha(\omega)$ in the UV region.

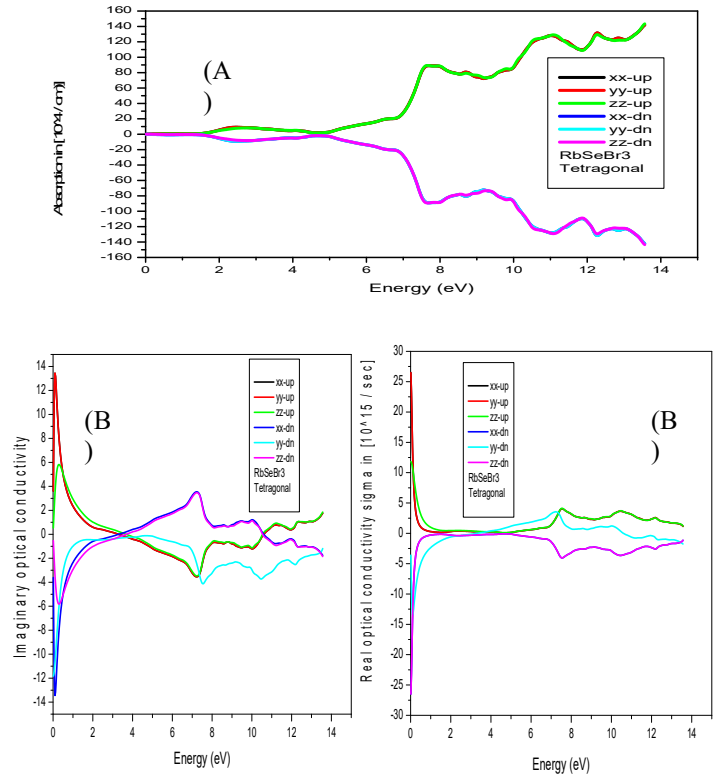


Fig. 7. (A) absorption spectra $\alpha(\omega)$, (B) Real and Imaginary optical conductivity of RbSeBr3.

The following expression in Eq. 9 sheds light on how an EM beams or light moves through a compound.

$$N(\omega) = n(\omega) + i k(\omega) \quad (9)$$

$n(\omega)$ represents the absolute refractive index and $k(\omega)$ represents the extinction coefficient. Figure 8 (A) shows the $n(\omega)$ curves. It details how much incident light is refracted or bent on its way through the material [28,29]. The maximum at 0 eV is 85 along yy and 58 along xx and zz axes, and then decreases to almost 0 in both visible and ultraviolet.

The values of the extinction coefficient $k(\omega)$ in Fig.8(B) provide information regarding the propagation depth of the EM wave's emergent photons as they move through the compound. The graph indicates that the $k(0)$ value is 95 along yy and 63 along xx and zz axes, and then in the visible and UV sections it is almost lining with the previous graph. Fig. 8(C) illustrates how an incident EM beam causes the loss of energy of electrons in a compound. We can learn about the plasmonic excitations from the $L(\omega)$ spectra [30], from which we infer that the energy loss truly results from electronic excitations. The EELS plot reveals that the UV zone, where it reaches the largest peak of the compound, contains the majority of the losses. Next, we estimated the reflectivity $R(\omega)$ spectra, which are displayed in Fig. 8 (D), where we can see that the reflectivity decreases in the visible region and then increases as the energy level rises in the UV interval.

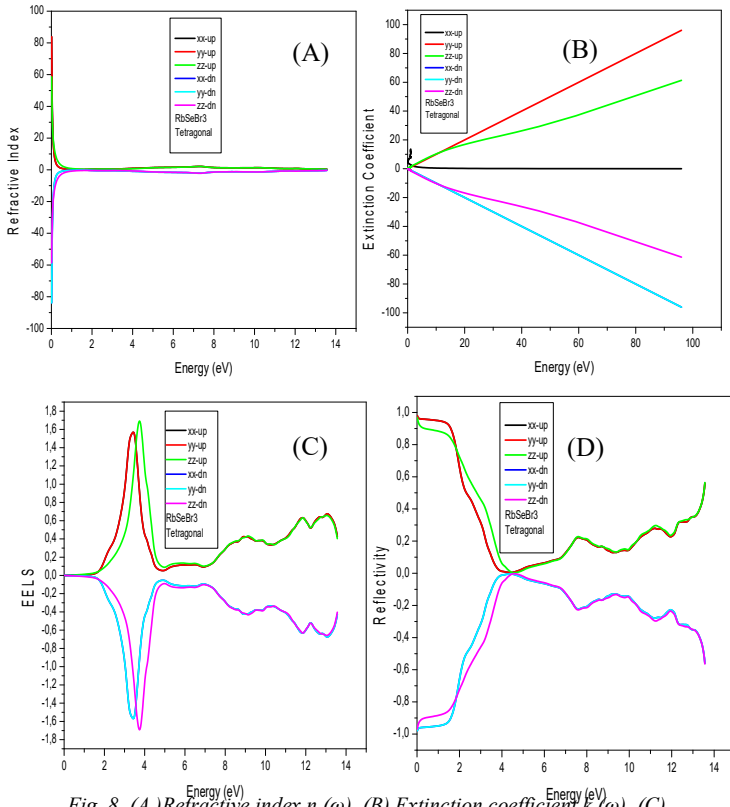


Fig. 8. (A) Refractive index $n(\omega)$, (B) Extinction coefficient $k(\omega)$, (C) Electron energy loss function $L(\omega)$ and (D) Reflectivity $R(\omega)$ of RbSeBr3.

4. THERMOELECTRIC PROPERTIES

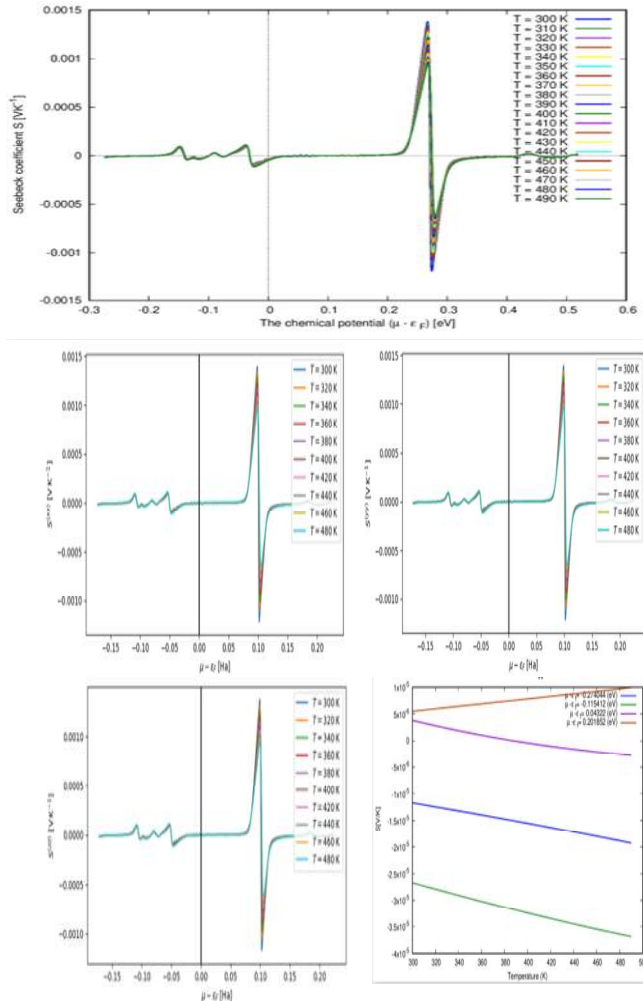


Fig.9. Seebeck coefficient of RbSeBr3

Finally, the thermoelectric (TE) properties Seebeck coefficient (S), electrical conductivity per relaxation time (σ/τ), and power factor (PF) were investigated. These were calculated based on chemical potentials (μ) in the energy range 0.25–0.5 eV at temperatures between 300–500 K.

The magnitude of the thermoelectric voltage caused by the temperature difference in the connection is described by the Seebeck coefficient (S). The nature of the dominant carrier is indicated by the letter S [22]. The largest peak of S occurs at 14 mV/K, 0.25 eV at a temperature of 300 K, and the peak value of S varies with temperature. Figure 9 shows the variation of S with chemical potential and temperature along the xx, yy and zz axes.

Figure 10 shows the conductivity per relaxation time (σ/τ) as a function of μ . This metric provides information on the electrical conductivity of a material produced by the flow of electrons along a temperature gradient from hot to cold. From the peak values of σ/τ plotted against μ , it can be observed that they do not change significantly with temperature. The highest value is $\sim 6.2 \Omega/\text{ms}$ at 300K.

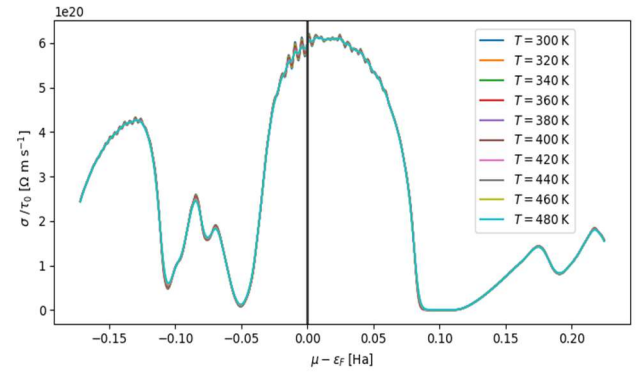


Fig.10. The electrical conductivity per relaxation time (σ/τ) as a function of μ of RbSeBr3

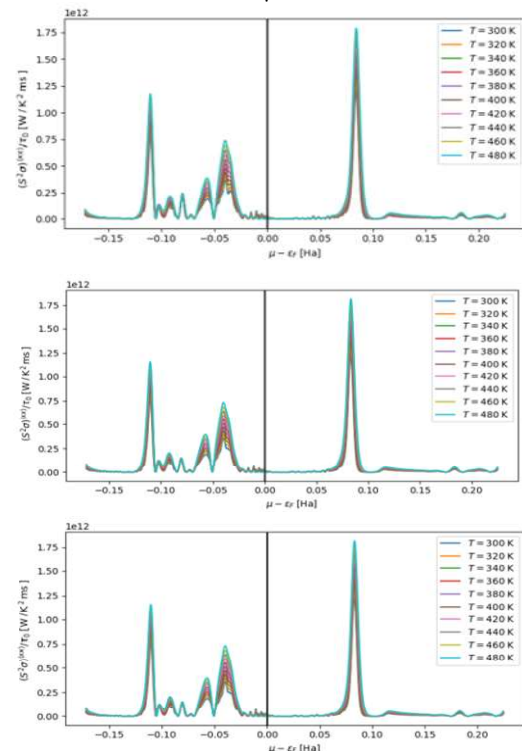


Fig.11. Power Factor of the Tetragonal RbSeBr3

The material's power factor (P.F.) is a crucial indicator of how effective its thermoelectric properties are. The feature is directly dependent on the Seebeck coefficient and electrical conductivity, as seen by the expression $P.F = S^2\sigma/\tau$ [22]. The plots of P.F. with respect to μ are presented in Fig. 11. From 300 K to 500 K, the power factor increases, reaching a high value of 1.8 W/K²ms at 0.8 Ha at 480 K.

IV. CONCLUSION

The halide perovskite RbSeBr₃ reported in this work was ultimately explored to establish its structural, electronic, optical, and thermoelectric properties using the FP-LAPW method. The findings indicate that RbSeBr₃ lacks an energy band gap and behaves like a metal. Indeed, the Fermi level is dominated by a high hybridization of Se-p states and Br-p states. The high absorption peaks at (2.8, 7.8, and 11eV) demonstrate the effectiveness of this material in the UV range. It is considered as an absorber in the UV range and can be used in sensitive devices to protect against harmful UV radiation. Furthermore, the investigated thermoelectric properties suggest using RbSeBr₃ as appropriate for thermoelectric power generators.

REFERENCES

- [1] Gratzel, M. (2014). The light and shade of perovskite solar cells. *Nat. Mater.* 13, 838–842.
- [2] Green, M.A., Ho-Baillie, A., and Snaith, H.J. (2014). The emergence of perovskite solar cells. *Nat. Photon.* 8, 506.
- [3] Liu, M., Johnston, M.B., and Snaith, H.J. (2013). Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* 501, 395.
- [4] Correa-Baena, J.P., Saliba, M., Buonassisi, T., Gratzel, M., Abate, A., Tress, W., and Hagfeldt, A. (2017). Promises and challenges of perovskite solar cells. *Science* 358, 739–744.
- [5] Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* 131, 6050–6051.
- [6] National Center for Photovoltaics, Best Research-Cell Efficiencies, National Renewable Energy Laboratory, <https://www.nrel.gov/pv/assets/images/efficiencychart.png>.
- [7] H. L. Bowman, On the structure of perovskite from the burgumer Alp, *Pfischthal, Tyrol. Mineral. Mag.* 1908, 15, 156–176.
- [8] H. F. Kay and P. C. Bailey. "Structure and Properties of CaTiO₃". *Acta Cryst.* (1957), 10, 219.
- [9] V. M. Goldschmidt, Die Gesetze der Krystallochemie. *Naturwissenschaften* 1926, 14, 477–485.
- [10] V. M. Goldschmidt, Titanium pigment and process of producing the same. 1922.
- [11] E. Wainer, High titania dielectrics. *J. Electrochem. Soc.* 1946, 89, 331–356.
- [12] R. Miyake and S. Ueda, On polymorphic change of BaTiO₃. *J. Phys. Soc. Jpn.* 1946, 1, 32–33.
- [13] The Materials Project, 36 MATERIALS SCIENCE, LBNL United States, (2020).
- [14] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, wien2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal properties (Vienna University of Technology, Vienna, Austria, 2001).
- [15] W. Kohn and L. J. Sham, *Phys. Rev. A* 1133, 140, 1965.
- [16] K. Schwarz and P. Blaha, "Solid state calculations using WIEN2k," *Comput. Mater. Sci.*, vol. 28, no. 2, pp. 259–273, 2003.
- [17] J.P. Perdew, Y. Wang, *Phys. Rev. B* 1992;45:13244.
- [18] F. Tran, P. Blaha, *Phys. Rev. Lett.* 102 (2009), 226401.
- [19] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, An Augmented PlaneWave Plus Local Orbitals Program for Calculating crystals Properties..(2008)
- [20] J. Anubhav, O. S. Ping, H. Geoffroy, C. Wei, Richards, W. Davidson, D. Stephen, C. Shreyas, G. Dan, S. David and C. Gerbrand, P. Kristin. *APL Materials*, p. 011002. 1, 2013.

- [21] F. D. Murnaghan, "The Compressibility of Media under Extreme Pressures," *Proceedings of the National Academy of Sciences of the USA*, Vol. 30, No. 9, 1944, pp. 244–247.
- [22] R. Sharma, A. Dey, S. A. Dar and V. Srivastava, A DFT investigation of CsMgX₃, India (2021).
- [23] G.J. Snyder, E.S. Toberer, *Nat. Mater.* 7 (2008) 105.
- [24] V Kumar, A Dey, S Thomas, M.A. Zaeem, D.R Roy, *Phys. Chem. Chem. Phys.* 23 (2021) 10409–10417.
- [25] J. Bechhoefer, Kramers–kronig, bode, and the meaning of zero, *Am. J. Phys.* 79(2011) 1053–1059.
- [26] C.C. Kim, J. Garland, P. Raccach, Modeling the optical dielectric function of the alloy system Al x Ga 1- x as, *Phys. Rev. B* 47 (1993) 1876.
- [27] S.A. Dar, R. Sharma, V. Srivastava, U.K. Sakalle, *RSC Adv.* 9 (2019) 9522.
- [28] V Kumar, A Dey, S Thomas, M.A. Zaeem, D.R Roy, *Phys. Chem. Chem. Phys.* 23 (2021) 10409–10417.
- [29] H.M. Ghaithan, Z.A. Alahmed, S.M.H. Qaid, M. Hezam, A.S. Aldwayyan, *ACS Omega* 5 (2020) 7468.
- [30] G.J. Snyder, E.S. Toberer, *Nat. Mater.* 7 (2008) 105.



Rabah Mehyaoui was born on 16/12/1998 in Sidi Bel Abbès, ALGERIA. Graduated as a secondary school teacher (PES) field: Physics from ENS Taleb Abderrahmane, Laghouat, ALGERIA. Also a Master degree in: materials Physics from Djillali Liabes University, Sidi Bel Abbès, ALGERIA. Currently working as a high school teacher in Sidi Bel Abbès, Algeria, and a PHD student within the Materials Science and Applications Laboratory (LSMA) at the University of Ain Temouchent, Belhadj Bouchaib, Ain Temouchent, Algeria.

Catalytic pyrolysis of high-density polyethylene for the production of carbon nanomaterials: effect of pyrolysis temperature

Salma Belbessai, El-Hadi Benyoussef, and Nicolas Abatzoglou

Abstract— A two-stage reaction process is followed to convert high-density polyethylene (HDPE) into carbon nanofilaments (CNFs) and hydrogen-rich gas. The experiments are performed in a continuous mode in a two-stage quartz reactor: thermal pyrolysis of HDPE followed by the catalytic decomposition of the pyrolysis gases over a nickel catalyst prepared from mining residues. To examine the effect of the pyrolysis temperature on the yield and quality of the final products, two steps were followed. First, non-catalytic pyrolysis experiments were run at different temperatures (600, 650, and 700 °C), and the products were examined. Second, pyrolysis–catalysis experiments were performed at the same pyrolysis temperatures and a fixed catalytic temperature (600 °C) to examine the CNF and hydrogen yields. The results showed that the production of carbon nanomaterials (CNMs) and H₂ is optimal at 650 °C, with yields of 70.8 and 38.0 wt%, respectively. Scanning electron microscopy (SEM) revealed the presence of carbon filaments with different diameters and lengths at the three different temperatures. Moreover, thermogravimetric analysis (TGA) confirmed that the produced carbon is filamentous, with the presence of amorphous carbon at 700 °C.

Keywords – Carbon nanomaterial, pyrolysis, catalysis, high-density polyethylene, hydrogen.

NOMENCLATURE

CNF	Carbon nanofilament
CNM	Carbon nanomaterial
CNT	Carbon nanotube
HDPE	High-density polyethylene
MWCNT	Multi-walled carbon nanotube
PET	Polyethylene terephthalate
SEM	Scanning electron microscopy
SLPM	Standard Liter Per Minute
TGA	Thermogravimetric analysis
UGSO	UpGraded slug oxides

I. INTRODUCTION

The continuous demand for plastic across the world has led to the accumulation of plastic waste. Of the different ways to treat plastic waste, the mechanical recycling of mixed plastics is very limited as it deals with pure single-polymer streams. Polyethylene terephthalate (PET) is the only plastic that can be mechanically recycled in closed-loop circulation [1]. In addition, the incineration of plastic waste is a practice that has several drawbacks; burning waste polymers releases greenhouse gases and hazardous chemicals into the environment [2]. On the other hand, thermal cracking, such as

pyrolysis, is a promising alternative since it is more robust toward mixed and contaminated plastics. During pyrolysis, the waste polymers are thermally degraded, in the absence of oxygen, into liquids, gases, and solid residues.

One of the applications of pyrolysis is the production of carbon nanomaterials (CNMs), such as carbon nanotubes (CNTs) and carbon nanofilaments (CNFs). These materials are high-value products and can be used in several applications, acting as composite fillers, for example [3]. They can be synthesized in one- or two-step processes: in the former, pyrolysis and catalytic cracking occur in the same reactor, while in the latter, they take place in two separate reactors [4]. The second configuration is favoured as it avoids catalyst poisoning [5].

Both the pyrolysis and catalysis temperatures have an impact on CNM production. Liu et al. [6] investigated the effect of temperature during the conversion of polypropylene (PP) into multi-walled carbon nanotubes (MWCNTs), finding that the composition of the pyrolysis gas changed with the temperature. The concentrations of H₂, CH₄, and C₂H₄ increased with the temperature, and the concentrations of the C₃ and C₄ alkenes reached a maximum at 650 °C. The MWCNT yield followed the same trend of propylene and butylene. From 550 to 650 °C, the MWCNT yield increased because the overall amount of gas increased; however, when the temperature exceeded 650 °C, the alkenes decreased, leading to a decrease in the MWCNT yield. This is expected as unsaturated compounds produce more CNTs than methane. The effect of catalytic temperatures on the quality and quantity of CNMs has been widely studied in the reported literature; however, studies on the effect of the pyrolysis temperature are lacking.

This work aims to investigate the effect of the pyrolysis temperature on the yield of CNFs produced during the pyrolysis–catalysis of used high-density polyethylene (HDPE). The pyrolysis products formed at different temperatures were examined and compared. Thereafter, the same experiments were conducted in the presence of a catalyst in a two-stage reactor to compare the yields of the produced CNMs; the catalyst, Ni-UpGraded Slug Oxides (Ni-UGSO), is prepared

Manuscript received December 2, 2022; revised July 9, 2023.

S. Belbessai and E-H. Benyoussef are from Laboratoire de Valorisation des Énergies Fossiles, École Nationale Polytechnique. (e-mails: salma.belbessai.benyoussef@g.enp.edu.dz, Elhadi.benyoussef@g.enp.edu.dz)

N. Abatzoglou is with department of chemical and Biotechnological Engineering, Université de Sherbrooke, Sherbrooke, CANADA (e-mails: Nicolas.abatzoglou@usherbrooke.ca).

Digital Object Identifier (DOI): 10.53907/enpesj.v3i1.177

from mining residues and has been proven to be efficient in CNF production [7].

II. MATERIALS AND METHODS

Used HDPE, with particle sizes varying from 3 mm to 1 cm, was obtained from KWI Solutions Polymers Inc. The plastic was used without further treatment. UGSO was provided by Rio Tinto Iron & Titanium, and the nickel nitrates were purchased from Sigma-Aldrich.

Ni-UGSO was prepared by incipient wetness impregnation. UGSO particles with sizes below 53 μm were mixed with nickel nitrates and droplets of water, with the Ni loading at 10 wt%. The mixture was dried for 3 h at 105 $^{\circ}\text{C}$ and subsequently calcined for 16 h at 900 $^{\circ}\text{C}$. Finally, the particles were crushed and sieved to recover those smaller than 53 μm in size.

The pyrolysis and pyrolysis-catalysis experiments were performed in a two-stage fixed-bed quartz reactor. In the pyrolysis experiments, quartz wool was placed in the middle of the reactor to receive the waste plastic fed by a two-stage feeder at a rate of 0.33 $\text{g} \cdot \text{min}^{-1}$. The temperature in both stages was the same, and N_2 flowed through the reactor at a rate of 0.03 SLPM to clear out the pyrolysis gases. In the pyrolysis-catalysis experiments, the degradation of HDPE occurred in the first stage, followed by catalytic cracking in the second stage. For each experiment, 5 g of catalyst was dispersed in quartz wool positioned in the catalytic zone. Another piece of quartz wool was placed in the middle of the setup in the first stage for the pyrolysis reaction. In these experiments, the catalyst was activated with H_2 at a flow rate of 0.10 SLPM for 3 h at 600 $^{\circ}\text{C}$. The duration of each reaction was 2 h, and condensable liquids were recovered in a cold trap immersed in an ice bath. The gas exiting this condenser passed through a charcoal column to retain all possible liquid hydrocarbons. Samples of the gas were taken every 10 minutes for gas chromatography (GC) analysis using a SCION 456-GC equipped with FID and TCD detectors.

To examine the morphologies of the CNMs, scanning electron microscopy (SEM) micrographs were obtained using the Hitachi S-4700 field emission gun.

Thermogravimetric analysis (TGA) was used to quantify the amount of carbon deposited on the catalytic surface and detect the presence of amorphous carbon. The analysis was performed using a Setaram Setsys 24 analyzer under a stream of 20% O_2 and 80% Ar from room temperature to 1000 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$.

III. MATHS

The accumulated solids on the quartz wool and catalytic bed (catalyst on quartz wool) were weighed to estimate the yield of solid products, Y_{solid} , as given by Equation 1:

$$Y_{\text{solid}}(\text{wt}\%) = \frac{m_{\text{solid}}}{m_{\text{plastic}}} \times 100 \quad (1)$$

The cold trap and the adsorbent were also weighed to determine the yield of the liquids and wax, Y_{liquids} , as given by Equation 2:

$$Y_{\text{liquids}}(\text{wt}\%) = \frac{m_{\text{liquids+wax}}}{m_{\text{plastic}}} \times 100 \quad (2)$$

The gas yield, Y_{gas} , was determined according to Equation 3:

$$Y_{\text{gas}}(\text{wt}\%) = 100 - Y_{\text{liquids}} - Y_{\text{solid}} \quad (3)$$

The yield of filamentous carbon was determined as in Equation 4:

$$Y_{\text{filamentous carbon}}(\text{wt}\%) = \frac{m_{\text{filamentous carbon}}}{m_{\text{carbon contained in the plastic}}} \times 100 \quad (4)$$

The yield of hydrogen was determined as in Equation 5:

$$Y_{\text{hydrogen}}(\text{wt}\%) = \frac{m_{\text{hydrogen}} \times 2}{m_{\text{hydrogen contained in the plastic}}} \times 100 \quad (5)$$

IV. RESULTS AND DISCUSSION

A. Effect of temperature on pyrolysis products

Table I shows the product distribution for the pyrolysis experiments at different temperatures. As the pyrolysis temperature increases from 600 to 700 $^{\circ}\text{C}$, the amount of pyrolysis gas increases significantly from 37.0 to 79.0 wt%, the liquid yield decreases significantly from 62.3 to 20.0 wt%, and the solid yield changes slightly. These results are similar to those obtained during the pyrolysis of polyethylene (PE) in a fixed-bed reactor [8]. The gaseous stream is mainly composed of H_2 , CH_4 , C_2H_4 , and C_2H_6 . Both H_2 and CH_4 have optimum yields – 25.8 and 51.3 vol%, respectively – at 650 $^{\circ}\text{C}$, while C_2H_4 and C_2H_6 follow the opposite trend, with minimum yields at 650 $^{\circ}\text{C}$. As the temperature increases from 600 to 650 $^{\circ}\text{C}$, the production of light components increases, while increasing the temperature further to 700 $^{\circ}\text{C}$ leads to further cracking of the HDPE and the generation of more gaseous products.

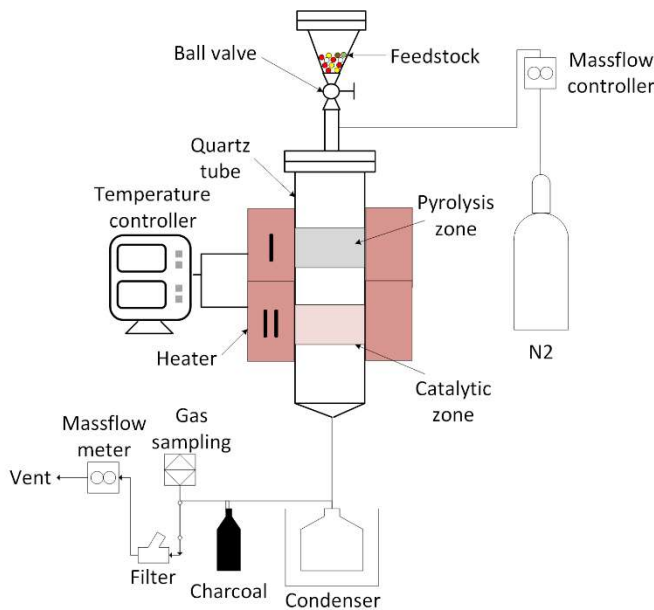


Fig. 1: Schematic diagram of the experimental setup

Table. I

PRODUCT DISTRIBUTION AND GAS COMPOSITION FROM PYROLYSIS OF HDPE
AT DIFFERENT TEMPERATURES

Temperature (°C)	600	650	700
Solid yield (wt%)	0.7	3.2	1.0
Gas yield (wt%)	37.0	58.3	79.0
Liquid yield (wt%)	62.3	38.5	20.0
Gas composition (vol%)			
H ₂	11.2	25.8	16.77
CH ₄	39.9	51.3	45.8
C ₂ H ₄	36.7	19.2	30.9
C ₂ H ₆	12.1	3.5	6.4

Fig. 2 shows the mass yields of the main products from the pyrolysis of HDPE at different temperatures. The liquid fraction mainly contains unsaturated C₇–C₉ and saturated C₁₂ hydrocarbons. These components decrease with the temperature, which is expected as the liquid yield decreases from 62.3 to 20.0 wt%. The mass yield of C₂H₄ decreases from 39.5 to 20.6 wt% as the temperature increases from 600 to 650 °C, and it increases to 37.3 wt% as the temperature reaches 700 °C. The mass yields and volumetric compositions (Table I) of CH₄ and C₂H₄ follow the same trends.

HDPE decomposes following the random chain scission mechanism [9]. The process involves several steps, including initiation, propagation and/or free radical transfer, and termination. The monomer is produced during the propagation reactions, while hydrogen abstraction occurs in the free radical transfer reactions, resulting in the formation of one saturated and one unsaturated end and a new free radical [10]. When intramolecular hydrogen transfer is favoured, the process leads to an increase in the production of olefins, while intermolecular transfer increases the paraffins [11]. From Fig. 1, one can note that at 600 °C, the production of olefins is favoured, which decreases when the temperature is increased to 650 °C. This indicates that at 600 °C, intramolecular hydrogen transfer is dominant.

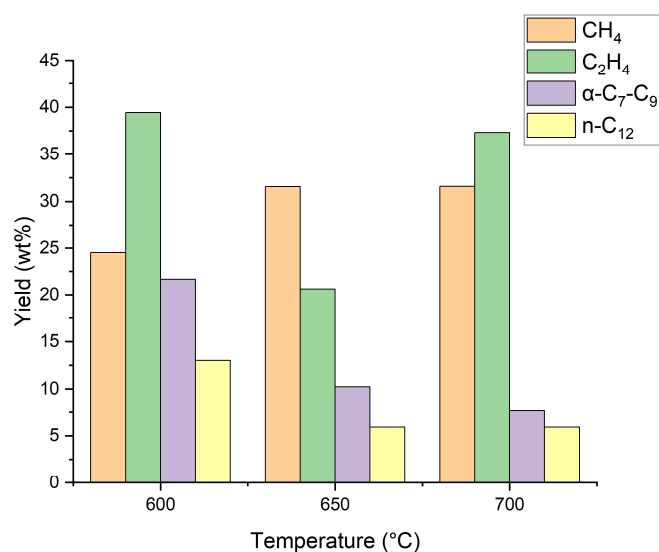


Fig. 2: Mass yields of the main products from the pyrolysis of HDPE at different temperatures.

B. Pyrolysis–catalysis of used HDPE

Table II presents the results of the pyrolysis–catalysis of used HDPE using Ni-UGSO at different temperatures. The total yield of filamentous carbon varies between 40 and 71 wt%, with the maximum production at 650 °C. The yields of filamentous carbon and H₂ at this temperature are 70.8 and 38.0 wt%, respectively. Consequently, the rate of production of the former at this temperature is at its optimum (2.4 g_C·g_{cat}⁻¹·h⁻¹). Additionally, the amount of liquid residue is the lowest at 650 °C, with a yield of 9.5 wt%, whereas the gas yield at this temperature is similar to that at 700 °C. This indicates that the filamentous carbon is produced from the catalytic decomposition of mostly liquid hydrocarbons, such as α-C₇–C₉ and n-C₁₂. The gaseous stream is mainly composed of H₂.

One would expect greater production of filamentous carbon at 600 °C because of the large presence of unsaturated hydrocarbons, as explained in Section IV.A. However, the results reveal that the optimum production occurs at 650 °C. The growth of CNMs depends on several parameters, such as the pyrolysis and catalytic temperatures, metal particle size, and type of feedstock. All these factors influence the process interdependently [5].

Table. II

CNM AND H₂ YIELDS FROM PYROLYSIS–CATALYSIS OF HDPE USING Ni-UGSO AT 600, 650, AND 700 °C AND A FIXED CATALYSIS TEMPERATURE (600 °C)

Temperature (°C)	600	650	700
Solid yield (wt%)	37.3	59.6	46.5
Gas yield (wt%)	43.5	30.9	33.9
Liquid yield (wt%)	19.2	9.5	19.6
Filamentous carbon production rate (g _C ·g _{cat} ⁻¹ ·h ⁻¹)	1.5	2.4	1.8
Total filamentous carbon yield (wt%)	44.1	70.8	55.1
Total H ₂ yield (wt%)	27.2	38.0	32.5
Gas composition (vol%)			
H ₂	57.2	73.5	65.5
CH ₄	39.2	22.4	24.1
C ₂ H ₄	9.1	5.5	4.3
C ₂ H ₆	2.8	1.8	5.7

SEM images of Ni-UGSO after the reaction at the different pyrolysis temperatures are shown in Fig. 3. The produced carbon is crystalline and in the form of filaments of different diameters and lengths. At 600 °C, more filaments with larger diameters are present. Crystals of the catalyst are also visible, indicating that the form of CNF does not considerably affect the access of the reactants to the surface of the catalyst. The metal particles are located at the top of the nanofilament.

Fig. 4 shows the derivative plots of the TGA of the spent Ni-UGSO at the different pyrolysis temperatures. At 600 and 650 °C, the weight loss occurs at 615 °C, and only one peak is present in each plot. On the other hand, the plot at 700 °C presents two peaks, one at 590 and the other at 650 °C. The higher the crystallinity of the carbon, the higher the oxidation temperature [4]. This indicates that the carbon produced at 600 and 650 °C is mostly crystalline, while that produced at 700 °C is a mixture of filamentous and amorphous carbon.

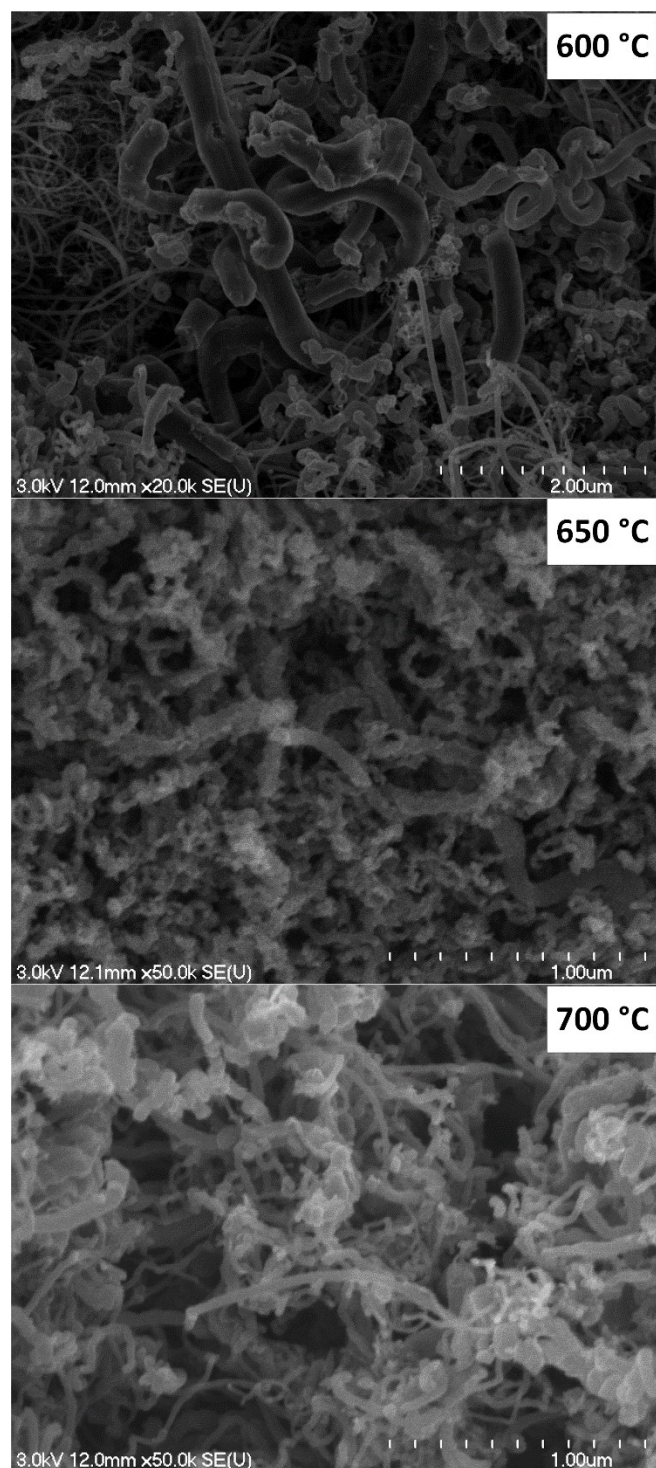


Fig. 3: SEM images of the carbon produced at different pyrolysis temperatures.

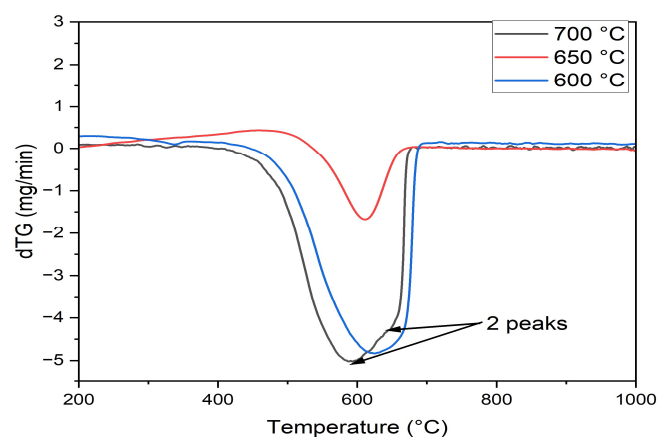


Fig. 4: Derivative plots of the TGA of spent Ni-UGSO at different temperatures.

V. CONCLUSION

The pyrolysis temperature affects the quantity and composition of the pyrolysis products and the yield of CNMs. The optimum production of CNMs and H_2 , with yields of 70.8 and 38.0 wt%, respectively, occurs at 650 °C. The liquid yield is the lowest at this temperature, which indicates that the long-chain hydrocarbons are further cracked in the presence of Ni-UGSO to form filamentous carbon.

TGA revealed that the carbon produced at 600 and 650 °C is mostly filamentous, while there is an indication of the presence of amorphous carbon at 700 °C. This indicates that the pyrolysis temperature also affects the quality of the carbon produced.

ACKNOWLEDGMENTS

The authors would like to thank the University of Sherbrooke's Plateforme de Recherche et d'Analyse des Matériaux (PRAM). We thank Karen Bechwaty and Mohamed Hossam Eldakamawy for their technical support.

REFERENCES

- [1] M. Kusenberg, A. Zayoud, M. Roosen, H. Dao, M.S. Abbas-abadi, A. Eschenbacher, U. Kresovic, S. De Meester, K.M. Van Geem, A comprehensive experimental investigation of plastic waste pyrolysis oil quality and its dependence on the plastic waste composition, *Fuel Process. Technol.* 227 (2022) 107090. <https://doi.org/10.1016/j.fuproc.2021.107090>.
- [2] M.M. Harussani, S.M. Sapuan, U. Rashid, A. Khalina, R.A. Ilyas, Pyrolysis of polypropylene plastic waste into carbonaceous char: Priority of plastic waste management amidst COVID-19 pandemic, *Sci. Total Environ.* 803 (2022) 149911. <https://doi.org/https://doi.org/10.1016/j.scitotenv.2021.149911>.
- [3] C. Wu, M.A. Nahil, N. Miskolczi, J. Huang, P.T. Williams, Production and application of carbon nanotubes, as a co-product of hydrogen from the pyrolysis-catalytic reforming of waste plastic, *Process Saf. Environ. Prot.* 103 (2017) 107–114. <https://doi.org/10.1016/j.psep.2016.07.001>.
- [4] S. Belbessai, E. Benyoussef, F. Gitzhofer, N. Abatzoglou, Carbon nanomaterial production using waste plastic pyrolysis over a new catalyst made from mining residues: Effect of plastic type, *Chem. Eng. J. Adv.* 12 (2022) 100424. <https://doi.org/10.1016/j.cej.2022.100424>.
- [5] A. Azara, S. Belbessai, N. Abatzoglou, A review of filamentous carbon nanomaterial synthesis via catalytic conversion of waste plastic pyrolysis products, *J. Environ. Chem. Eng.* 10 (2022) 107049. <https://doi.org/10.1016/j.jece.2021.107049>.
- [6] J. Liu, Z. Jiang, H. Yu, T. Tang, Catalytic pyrolysis of polypropylene to synthesize carbon nanotubes and hydrogen through a two-stage process, *Polym. Degrad. Stab.* 96 (2011) 1711–1719. <https://doi.org/10.1016/j.polymdegradstab.2011.08.008>.
- [7] A. Azara, E. Benyoussef, F. Mohellebi, M. Chamoumi, Catalytic Dry Reforming and Cracking of Ethylene for Carbon Nanofilaments and Hydrogen Production Using a Catalyst Derived from a Mining Residue, *Catalysts*. 9(12) (2019) 1069. <https://doi.org/https://doi.org/10.3390/catal9121069>.
- [8] S. Jung, M. Cho, B. Kang, J. Kim, Pyrolysis of a fraction of waste polypropylene and polyethylene for the recovery of BTX aromatics using a fluidized bed reactor, *Fuel Process. Technol.* 91 (2010) 277–284. <https://doi.org/10.1016/j.fuproc.2009.10.009>.
- [9] S. Belbessai, A. Azara, N. Abatzoglou, Recent Advances in the Decontamination and Upgrading of Waste Plastic Pyrolysis Products: An Overview, *Processes*. 10 (2022) 733. <https://doi.org/https://doi.org/10.3390/pr10040733>.
- [10] A. Marcilla, M.I. Beltrán, R. Navarro, Thermal and catalytic pyrolysis of polyethylene over HZSM5 and HUSY zeolites in a batch reactor under dynamic conditions, *Appl. Catal. B Environ.* 86 (2009) 78–86. <https://doi.org/10.1016/j.apcatb.2008.07.026>.
- [11] S.M. Al-salem, Thermal pyrolysis of high density polyethylene (HDPE) in a novel fixed bed reactor system for the production of high value gasoline range hydrocarbons (HC), *Process Saf. Environ. Prot.* 127 (2019) 171–179. <https://doi.org/10.1016/j.psep.2019.05.008>.

Salma Belbessai Ph.D. student at the Department of Chemical Engineering of the Université de Sherbrooke (Sherbrooke, Canada) and Ecole Nationale Polytechnique (Algiers, Algeria). Research interests: thermochemical conversion of organic matter.

El-Hadi Benyoussef Titular professor at Ecole Nationale Polytechnique (Algiers, Algeria) and director of the Laboratoire de Valorisation des Énergies Fossiles. Research interests: essential oils extraction and modelling of chemical processes.

Nicolas Abatzoglou Titular professor at the Université de Sherbrooke (Sherbrooke, Canada) and director of the Groupe de Recherche sur les Technologies et Procédés (GRTP). Research interests: reactors for the thermochemical conversion of organic matter; particle systems; and the environment.