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Communication

Synthesis and characterization of NiO nanoparticles using *Manihot esculenta* aqueous extracts

B. Escobar [1,*], M. A. Lucio-García [2], Romeli Barbosa [3], D. Morales-Acosta [4]

[1] CONACYT, Centro de Investigación Científica de Yucatán, Mérida, Yucatán, 97302, México; beatriz.escobar@cicy.mx
[2] Universidad Autónoma de Yucatán, Mérida, Yucatán, 97069, México; monica.lucio@correo.uady.mx
[3] Universidad de Quintana Roo, Chetumal, Quintana Roo, 77019, México; romeli@uqroo.edu.mx
[4] CONACYT, Centro de Investigación en Química Aplicada, Saltillo, Coahuila, 25294, México; diana.morales@ciqa.edu.mx

* Correspondence: beatriz.escobar@cicy.mx; Tel.: +52-999-9300760

Abstract: Synthesis of nickel oxide nanoparticles (NiO NPs) is a low cost and ecofriendly route that brings great benefits over chemical and physical methods of synthesis. Our approach consisted of using aqueous extracts from treated waste of *Manihot Esculenta* (Cassava) as reducing, stabilizing and capping agents for the synthesis of NiO NPs. The results proved this approach might be a viable alternative. Extracts were mixed during 30 minutes with $Ni(NO_3)2.6H_2O$ leading to NPs formation. NiO NPs were characterized through FTIR, XRD, TEM and Raman spectroscopy. NiO NPs showed different shapes and sizes around 5-10 nm in agreement with the particle size calculated by XRD Scherrer equation.

Keywords: *Manihot esculenta*; nanoparticles; extracts

1. Introduction

Cassava (*Manihot esculenta Crantz*) is a versatile plant used as food, in pharmaceutical industry and fuel, due to its properties such as high purity, low cost, bio-compatibility and stability to form clear viscous pastes [1]. Cassava waste from regional markets contains about 40% starch and 11% cellulose [2], its poor management represents a problem because of the increasing of organic waste. Another use of cassava waste consists of feeding farm animals, which is a sustainable option in the short-term while new and different applications are found. Recently, green synthesis of nanoparticles (NPs) has risen as an ecofriendly alternative way to prepare NPs leading to the development of creative synthesis routes. Among the common approaches, the use of extracts from several kind of plants have shown positive results in the formation of NPs. Generally, the structure plant extracts is constituted by different metabolites like terpenoids, phenols, proteins or carbohydrates [3], these compounds are the direct responsible of the capability of the extract to carry out reduction/oxidation of NPs. Currently several types of metallic NPs have been synthesized from different solvents, used for the extraction of active compounds. It has been reported that the solvent polarity differences allow to obtain extracts with different chemical composition [4]. The NiO NPs have received considerable attention because of their applications as catalytic and magnetic materials [5] and medical applications [6]. According to the literature, the particle size, shape, and synthesis route of NiO NPs are key parameters to determine the catalytic behavior. The synthesis of NiO NPs using a cassava extract has been little explored, which awakened our interest in the current investigation. In this work, we prepared three different extracts using cassava waste for synthesis of NiO NPs.

2. Materials and Methods

Cassava waste was cut into pieces of one centimeter edge and dried at 80 °C overnight in an oven. The first extract named ExDCM included the use of HPLC grade dichloromethane as eluent. Technical grade ethanol was used as solvent in a 2:1 ratio with respect to the waste. Extracts were macerated during two days at room temperature. The solvent was filtered and eliminated with a rotary evaporator, subsequently solid-phase extraction was done. The second extract was obtained from solvothermal treatment (ST) of waste from cassava in the presence of Nejayote. The previous mixture was poured into an autoclave at 200 °C during 4 hours. When the process finished, we waited for the temperature to drop to 120 °C, the obtained solid was immersed in an ice bath. Then a centrifugation process was carried out at 6500 rpm for 10 minutes (ExNEJ). The third extract (ExAS) was obtained by the ST with the same conditions as ExNEJ, using H_2SO_4 a 0.2 M.

Three different materials of NiO NPs were synthesized, each one was prepared using 1 g-$Ni(NO_3)_2.6H_2O$ (nickel nitrate hexahydrate, 99.99% purity), mixed with 10 mL of cassava extracts during 30 min at 70° C until complete evaporation. Synthesized materials were placed inside a ceramic tube at 400°C during 4 hours in a nitrogen atmosphere. The temperature inside the furnace was monitored. The nomenclatures of the three samples obtained according to the extract used for the green synthesis of NiO NPs are NiDCM (dichloromethane), NiNEJ (nejayote) and NiAS (sulfuric acid).

The organic functional groups attached to the NPs chemical surface were determined by FTIR Spectroscopy (Tensor II, Bruker, 0.05 cm^{-1} resolution). Their structural analysis (size crystal and crystal planes) were characterized by X-Ray diffraction (XRD, D2 Phaser Bruker) in the area 20°–100° 2θ and a 0.02° step. The Raman spectra were collected on a Thermo Scientific DXR spectrometer using a 633 nm laser. NPs formation was confirmed by Transmission Electron Microscopy (TEM).

3. Results

3.1. Fourier transform infrared (FTIR)

Functional groups present in cassava extracts were analyzed by FTIR studies in the spectral range of 500-4000 cm^{-1}. Fig. 1a) shows the three different cassava extracts, where ExNEJ y ExAS show similar vibration bands, both of them exhibited an intense peak at 3200–3500 cm^{-1}, which corresponds to the chemical bond type O–H suggesting the presence of hydroxyl groups [7]. ExDCM spectrum shows a weak band around 1633 cm^{-1} which can be attributed to H-bonding and the interaction of hydroxyl groups [8]. ExDCM extract shows peaks around 2930 and 2852 cm^{-1} associated with C-H stretch vibrations [9]. The peaks around 1737-1060 cm^{-1} corresponding to the presence of ethers (1159 cm^{-1} due to C-O stretching) and halogens (1060 cm^{-1}, due to C-F stretching) [10] respectively. Fig.1b) shows FT-IR NiO NPs spectra prepared from the three cassava synthesized extracts. The broad band at 3400–3700 cm^{-1} corresponds to the stretching vibration mode of the chemically bonded hydroxyl group which is generally associated with phenols and carboxylic acids. It is worth noticing this band is weak for NiDCM which is in agreement with the use of DCM and the poor development of hydroxyl groups. Bands at 2100 and 1637 cm^{-1} are related to =CH and C=O stretching and -C=H bending vibrations which may indicate the presence of aldehyde groups, amides groups, and carboxylic acids [11]. It is interesting to observe that spectra of the solid samples are quite different, showing an effect on the synthesis of Ni and NiO NPs because of the extract used.

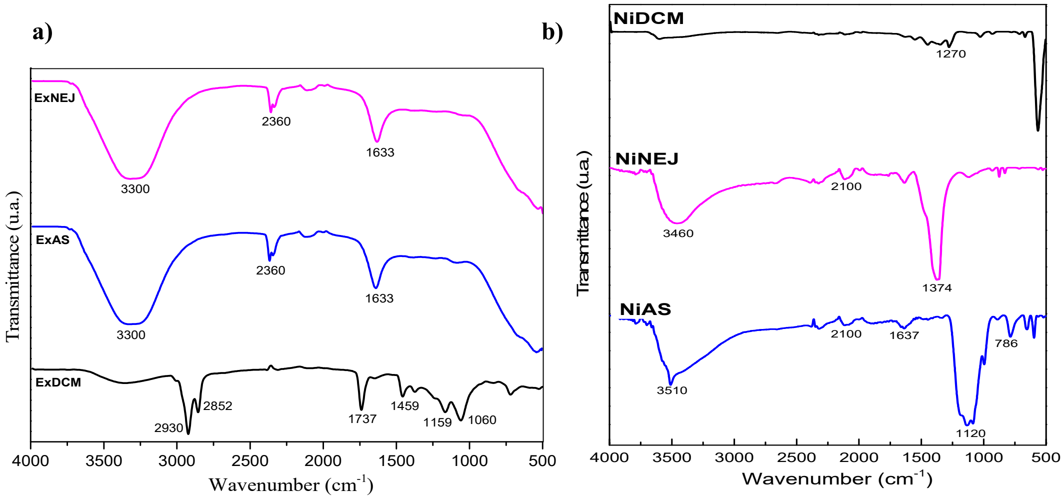

Fig. 1 FTIR spectra of a) Cassava extracts and b) NiO NPs prepared using Cassava extract.

3.2 X-Ray diffraction

Fig. 2a) shows XRD patterns obtained after the samples are calcined, this process enables to obtain Ni and NiO NPs, according to the extract used. NiO NPs samples have peaks at 37.2°, 43.2°, 62.8°, 75.4°, and 79.4° which can be attributed to the main characteristic of the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) crystal planes of face-centered cubic (fcc) nickel, respectively, and they were indexed in accordance with pattern diffraction file of NiO (PDF 04-01601090). Due to the characteristics of the process itself, extracts present available oxygen in the bulk, which would allow the oxidation process and NiO NPs formation. This phenomenon is also confirmed by FTIR analysis results, where the presence of carbon and oxygen promotes the formation of CO to CO_2 during the pyrolysis process [12]. NiDCM sample clearly shows Ni NPs formation, according to PDF 04-010-6148, and the results indicate a well-crystallized sample. The main NPS sizes were calculated by using Debye-Scherrer equation, resulting in 8.9, 7.9 and 8.2 nm for NiDCM, NiAS and NiNEJ, respectively.

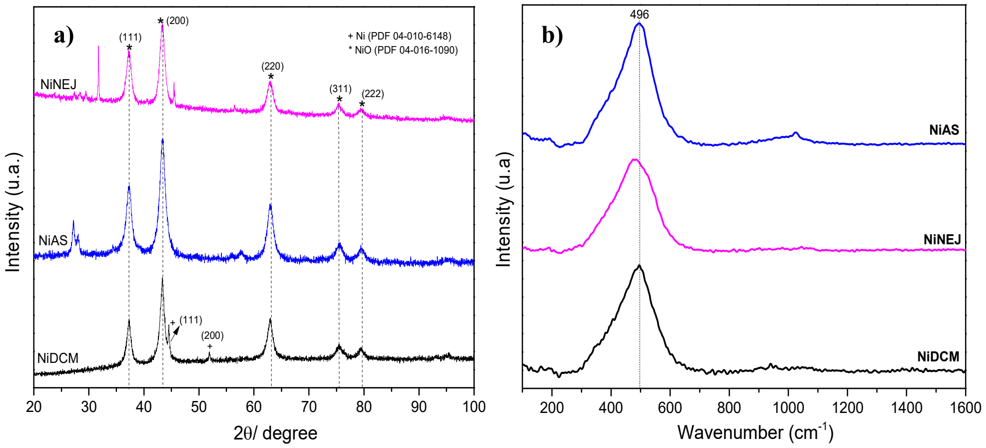

Figure 2 a) XRD patterns NiO NPs and b) typical Raman spectrums of the annealed NiO NPs at 400 °C for 4 h.

3.3 Raman analysis

Fig. 2b) shows Raman spectra for the three synthesized samples at 400 °C for 4 h, characteristic Raman bands at 496 cm^{-1} were identified. The Raman peaks at around 500 cm^{-1} belong to NiO according to the literature, and the main peak at 496 cm^{-1} shows NiO NPs dominant composition [13], confirming NPs formation from the three cassava extracts according to XRD studies discussed previously.

3.4 Transmission Electron Microscopy (TEM)

The morphology and structure of the Ni and NiO NPs were investigated by TEM. Different particle shapes and sizes were observed, as well as, the agglomeration during the particle formation was confirmed. NiDCM sample has an irregular formation with a particle size of around 9 nm. Whereas NiAS sample, shows a hexagonal shape confirmed in all three different synthesized NPs, about 7 nm. Finally, the NiNEJ sample presents a more sphere like formation with a particle size of around 9 nm. These results are in agreement with the crystalline sizes calculated though Scherrer formula, as seen above.

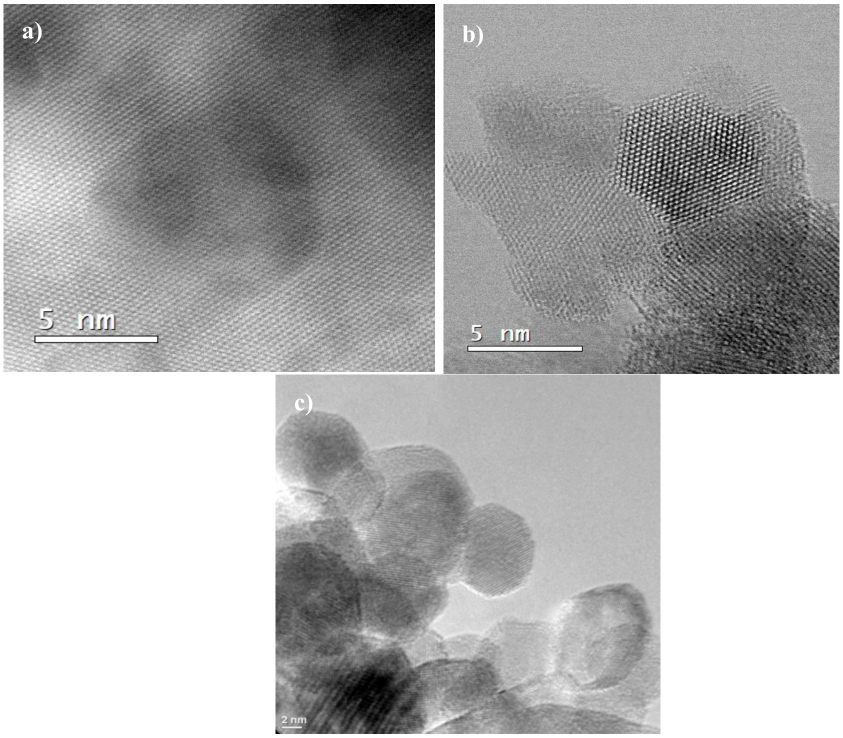

Figure 3 TEM NiO NPs images obtained using Cassava plant extract: a) NiDCM, b) NiAS and c) NiNEJ.

4. Conclusions

A novel green approach was proposed to synthesize Ni and NiO NPs using cassava extracts as reducing and capping agents. NPs formation was completed with heat treatment at 400 °C for 4 h.

XRD and TEM results showed NPs formation with particle sizes smaller than 10 nm. Raman analysis showed a band at 496 cm^{-1} validating NiO NPs formation. This work proposes a specific methodology for the synthesis of Ni and NiO NPs particles based on cassava extracts. However, other synthesis pathways can be expanded with different biomass extracts. Furthermore, NiO NPs obtained can be used as a catalytic converter for ORR in alkaline fuel cells.

Acknowledgments

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5. References

[1] X. Tan, B. Gu, X. Li, C. Xie, L. Chen, B. Zhang, Effect of growth period on the multi-scale structure and physicochemical properties of cassava starch, Int J Biol Macromol 101 (2017) 9-15. DOI: 10.1016/j.ijbiomac.2017.03.031.

[2] X. Xie, H. Xiong, Y. Zhang, Z. Tong, A. Liao, Z. Qin, Preparation magnetic cassava residue microspheres and its application for Cu (II) adsorption, J Environ Chem Eng 5 (2017) 2800-2806. DOI: 10.1016/j.jece.2017.05.024

[3] M. Martínez-Cabanas, M. López-García, J. L. Barriada, R. Herrero, M. E. Sastre de Vicente, Green synthesis of iron oxide nanoparticles. Development of magnetic hybrid materials for efficient As(V) removal, Chem Eng J 301 (2016) 83-91. DOI: 10.1016/j.cej.2016.04.149

[4] A. López-Córdoba, C. Medina-Jaramillo, D. Piñeros-Hernandez, S. Goyanes, Cassava starch films containing rosemary nanoparticles produced by solvent displacement method, Food Hydrocolloid 71 (2017) 26-34. DOI: 10.1016/j.foodhyd.2017.04.028

[5] Y. Han, S. Zhang, N. Shen, D. Li, X. Li, MOF-derived porous NiO nanoparticle architecture for high performance supercapacitors, Mater Lett 188 (2017) 1-4. DOI: 10.1016/j.matlet.2016.09.051

[6] K. Rajaram, D.C. Aiswarya, P. Sureshkumar, Green synthesis of silver nanoparticle using *Tephrosia tinctoria* and its antidiabetic activity, Mater Lett 138 (2015) 251-254. DOI:10.1016/j.matlet.2014.10.017

[7] A. Edhirej, S.M. Sapuan, M. Jawaid, N.I. Zahari, Cassava/sugar palm fiber reinforced cassava starch hybrid composites: Physical, thermal and structural properties, Int J Biol Macromol, 101 (2017) 75-83. DOI:10.1016/j.ijbiomac.2017.03.045

[8] L. Fama, A. M. Bittante, P. Sobral, S. Goyanes, L.N. Gerschenson, Garlic powder and wheat bran as fillers: Their effect on the physicochemical properties of edible biocomposites, Mater Sci Eng 30 (2010) 853-859. DOI:10.1016/j.msec.2010.03.022

[9] S. Mathew, M. Brahmakumar, T.E. Abraham, Microstructural imaging and characterization of the mechanical, chemical, thermal, and swelling properties of starch –chitosan blend films, Biopolymers 82 (2006) 176-187. DOI: 10.1002/bip.20480

[10] M.I. Din, A.G. Nabi, A. Rani, A. Aihetasham, M. Mukhtar, Single step green synthesis of stable nickel and nickel oxide nanoparticles from *Calotropis gigantea*: Catalytic and antimicrobial potentials, Environ. Nanotechnol. Monit. Manage, 9 (2018) 29-36. DOI: 10.1016/j.enmm.2017.11.005

[11] M. Kundu, G. Karunakaran, D. Kuznetsov, Green synthesis of NiO nanostructured materials using *Hydrangea paniculata* flower extracts and their efficient application as supercapacitor electrodes, Powder Technol 311 (2017) 132-136. DOI: doi.org/10.1016/j.powtec.2017.01.085

[12] Y.T. Foo , J.E Chan , G.C. Ngoh , A.Z. Abdullah , B.A. Horri, B. Salamatinia, Synthesis and characterization of NiO and Ni nanoparticles using nanocrystalline cellulose (NCC) as a template, Ceram Int 43 (2017) 16331-16339. DOI: doi.org/10.1016/j.ceramint.2017.09.006

[13] F.T. Thema, E. Manikandan, A. Gurib-Fakim, M. Maaza, Single phase Bunsenite NiO nanoparticles green synthesis by *Agathosma betulina* natural extract, J Alloys Compd 657 (2016) 655-661. DOI: doi.org/10.1016/j.jallcom.2015.09.227