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Original Research Article

A Friendly Environmental Route for the Fabrication of Spinel Co_3O_4 Nanorods, Using Inorganic Precursor Salt and Aqueous Extracts of *Moringa oleifera* Leaves

Gérard Niasa Mata[1], Joseph K'Ekuboni Malongwe[1], Pierre Osomba Lohohola[1], Jérémie Lunguya Muswema[1], Omer Muamba Mvele[1], Remy Imboyo Ndjoko[2], Hercule Mulonda Kalele[1], Désiré Kabuya Tshibangu[3*], Paul Kavuna Mahuku[4], Gracien Bakambo Ekoko[1]

[1]Department of Chemistry, Faculty of Science, University of Kinshasa, Kinshasa, Democratic Republic of the Congo, H8J5+7P7, Kinshasa, Congo - Kinshasa
[2]Department of Physical Chemistry, High Educational Institute of Kikwit, Kikwit, Democratic Republic of the Congo, XR6C+CRX, Kikwit, Congo - Kinshasa
[3]School of Materials Science and Engineering, HuaZhong University of Science and Technology, Wuhan, Hubei, People's Republic of China
[4]Department of prepolytechnics, Faculty of Polytechnics, University of Kinshasa, Kinshasa, Democratic Republic of the Congo, H8J5+7P7, Kinshasa, Congo - Kinshasa

***Corresponding Author:** Désiré Kabuya Tshibangu
School of Materials Science and Engineering, HuaZhong University of Science and Technology, Wuhan, Hubei, People's Republic of China

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Abstract: Nowadays many researchers are focused on the sytnhesis of nanoscale tricobalt tetraoxide (Co_3O_4) particles, owing to their unique properties. These particles have indeed many potential technological applications. The present investigation deals with the fabrication of this spinel oxide: it was successfully synthesized through a friendly environmental method, using cobalt (II) chloride as cobalt precursor and aqueous extract of *Moringa oleifera* leaves. The latter contains alkaloids as a base source while flavonoids present in the leaves acted as capping agent to prevent the particles agglomeration. Alkaloids present in the leaves were hydrolyzed in water and consequently, hydroxilated Co^{2+} leads to the formation of Co_3O_4 powder via calcination. The electronic transmission microscopy has revealed the single crystalline nanorods morphology of the synthetised materials. These nanorods are about several hundred nanometers long and several tens of nanometers in diameter. The bulk Co_3O_4 is known to be antiferromagnetic, the vibrating sample magnetometer data (at room temperature) of the prepared powder exhibited the lower coercivity and remanence, signaling that the produced spinel was pure and was constituted of superparamagnetic particles made of Co_3O_4. The UV–visible spectrum exhibited a photoluminescence peak in the visible light range positioned at about 538nm, suggesting this spinel as a visible light emitting material and as photocatalyst under visible light.

Keywords: Tricobalt tetraoxide, supermagnetic, *Moringa oleifera* leaves, aqueous extract.

1. INTRODUCTION

Nanotechnology is the science which is mainly concerned with the production, the manipulation and the use of materials at subatomic level in order to produce novel materials and processes [1, 2].

The synthesis of the spinel cobalt oxides, (Co_3O_4) nanoparticles has attracted the attention of many researchers, due to their unique particular properties as compared to their corresponding materials of macroscopic size. These materials have been reported to have some advantages and are used in microwave absorption [3], information storage and catalysts [4-7], and in electrochemitry for lithium ion batteries [8-12], magnetic material, sensors [13].

The spinel tricobalt tetraoxide, Co_3O_4 is a magnetic semiconductor, which is described by a formula unit AB_2O_4 [where, A is Co^{2+} and B is Co^{3+}]. This formula exhibits a normal spinel structure, where the tetrahedral A site is occupied by Co^{2+} and the octahedral B site by Co^{3+}. The oxygen ions are form a close-packed face centered cubic lattice [5].

Several conventional methods of fabricating Co_3O_4 nanorod particles have been reported in the litterature. These include, among others, Liquid-Phase Precipitation [14], co-precipitation method [15], hydrothermal synthesis [6, 10, 16], sol-gel method [17], thermal decomposition (in organic solvents) of organic cobalt precursor [18], gamma irradiation method [1], chemical preparation using utrasounds [19].

However, most of these physical and chemical fabrication routes of the spinel Co_3O_4 nanorod particles present a noticeable number of drawbacks [1]. Among these disadvantages, we enumerate the production high costs and high processing temperatures, the toxicity of the employed chemicals reagents, and the release of dangerous by-products.

It is well known that, the novel properties of Co_3O_4 materials are mostly dependent on their morphologies. Thus, there is, obviously, a need to develop synthetic methods which control the Co_3O_4 particles size and morphologies. The morphologies of the fabricated Co_3O_4, include structures such as spherical [1], nanoarrays [5], nanofibers [20], nanoboxes [12], nanotubes [13], nanorods [21] and hollow structure among others [11, 22].

Although the spinel Co_3O_4 nanostructure has been fabricated with different morphologies, the synthesis methods require in most cases, complicated techniques and rigorous synthesis conditions. In the present investigation, our attention has been focused on the production of cobalt oxide nanorods using an ecological, facile, rapid and non-toxic, synthesis pathway to fabricate in only one reaction step, tricobalt tetraoxide (Co_3O_4) nanorod particles, using aqueous extract of *Moringa oleifera* leaves and $CoCl_2.6H_2O$ as inorganic precursor. The synthesized powder product was characterized by X-ray diffraction (XRD), transmission electron microscopy (SEM), Fourier transform infrared (FT-IR) and others techniques.

2. MATERIALS AND METHODS

2.1. MATERIALS

The vegetable material, Moringa *oleifera* leaves were collected from the experimental garden of the department of Life Sciences, University of Kinshasa, Democratic Republic of the Congo (DRC). In order to avoid any photochemical degradation of these leaves from the sun light, they were dried for two weeks in the shade. The inorganic precursor salt, $CoCl_2.6H_2O$ (99% purity) and bidistilled water were supplied by Aldrich Chemicals.

2.2. Preparation of aqueous Extract

The preparation of water extrat consisted of mixing under magnetic stirring 30 g of *Moringa oleifera* leaves powder with 3000 mL of bidistilled water and the mixture was heated at 80 °C for about two hours. After filtration, the aqueous extracts were wrapped from the mixture and kept at 4 °C in the refrigerator.

2.3. Synthesis of Supermagnetic tricobalt tetraoxide nanorods

The $CoCl_2.6H_2O$ was used as the cobalt source. An aliquot of 50 mL of *Moringa oleifera* aqueous extract were mixed under magnetic stirring with 5g $CoCl_2.6H_2O$ for about one hour. To avoid photochemican parasite reaction, the solution was couvered by aluminium foil and kept in darkness for 18h. The solution was afterwards heated for 72 h at 120 °C. The obtained powder was purified by washing it several times and kept for 2 h at 500 °C.

2.4. Characterization techniques

All solvents and reagents need for tricobalt tetraoxide preparation and for analysis were commercially available and used directly without further purifications. The structure and the phase identification of the fabricated nanorod oxides were carried out using a diffractometer model, D/MAX-2550 X-ray (Cu-Kα radiation of $\lambda = 1.54056$ Å) with a nickel filter (Rigaku Co., Japan). A Fourier Transform Infrared spectrophotometer (SHIMADZU) using KBr pellet technique in the range from 4000 to 400 cm^{-1} was used to record the chemical bondings in Co_3O_4. The morphology and the rods size were determined by transmission electron microscopy (TEM; Hitachi H-800), and the micrographs were taken with an accelerating voltage of 200 kV with samples deposited on a carbon coated copper grid. The surface morphology, and elemental compositions of the oxide spinel Co_3O_4 were carried out using a field emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F) incorporated with an energy dispersive X-ray (EDAX) spectrophotometer with operating at 20 kV. The optical absorption measurements of the spinel were recorded using a UV–Vis spectrophotometer (Perkin Elmer) at the range between 200 and 900 nm. In order to obtain a homogeneous suspension, the powder sample was well dispersed in distilled water through sonication for 10 min. Finally, the magnetic measurements were recorded at room temperature using a vibrating sample magnetometer, model: BHV-55, Riken, Japan.

3. RESULTS AND DISCUSSION

3.1. XDR Phase evaluation

The phase composition of the as-prepared powder sample was examined by XRD. The X –ray diffraction pattern shown in Fig 1, revelead that all refraction peaks located at 2θ = 19 (111), 31 (220), 37 (311), 45 (400) and 66 (440), are well-matched with those given in the literature for cobalt oxide (JCPDS No. 42-1467) related to FCC cubic phase spinel Co_3O_4. No peak associated with cobalt metal appeared in the spetrum, suggesting that the fabricated spinel was completely pure.

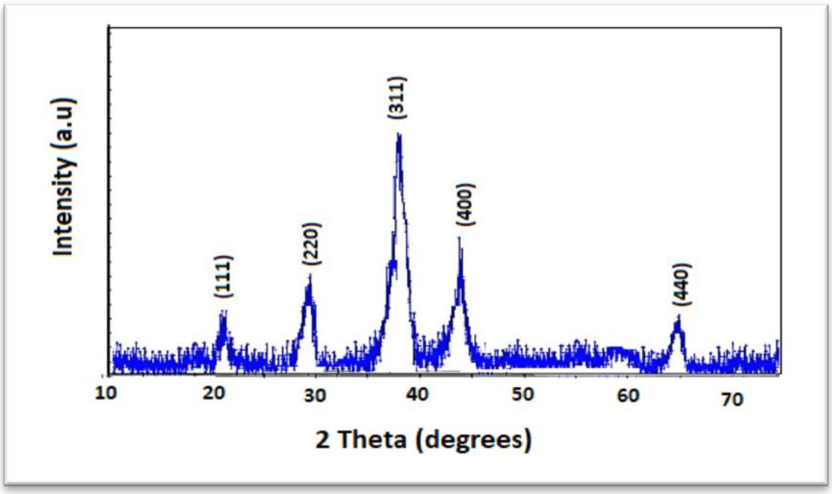

Fig 1: Diffractogram of cubic spinel Co_3O_4 powder synthesized from aqueous extrat of Moringa Oleifera leaves. Differents Bragg peaks are indexed by the corresponding Miller indices. Results were obtained using CuKα radiation (λ = 1.54178 Å)

3.2. TEM images

Before taking the TEM images of the biosynthesis sample, an ultrasonic vibration of dried powder of Co_3O_4 sample was made using absolute alcohol. Oxide sample was dispersed in solution, then an aliquot was transferred into the copper grid with carbon support film. Figure 2 shows the TEM image of the Co_3O_4 nanorods of several tens of nanometers in diameter and several hundred nanometers long, suggesting a catalytic application for the frabricated materials.

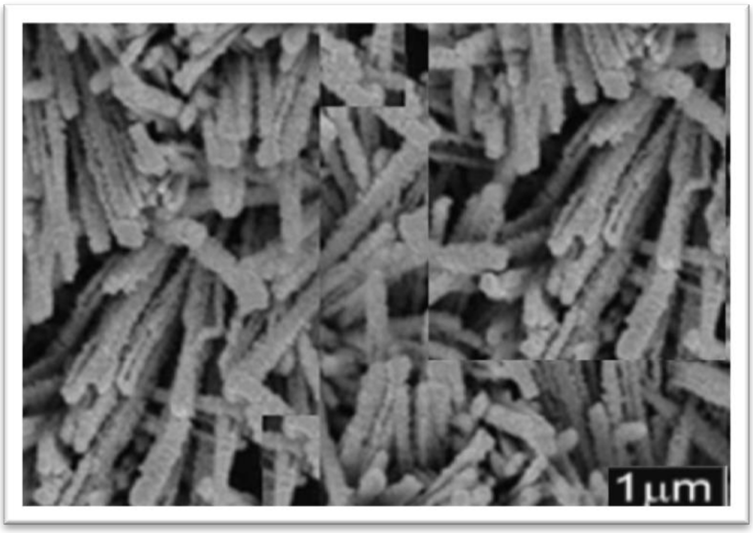

Fig 2: TEM image of the Co_3O_4 nanorodsgenerated from aqueous extract of Moringa Oleifera leaves

3.3. Energy dispersive studies (EDS)

EDS analysis of Co_3O_4 was achieved by using internal standard at energy from 0 keV to 10 keV. Energy dispersive spectrum (Fig 3) showed that the prepared powder is mainly constituted of cobalt and oxygen elements.

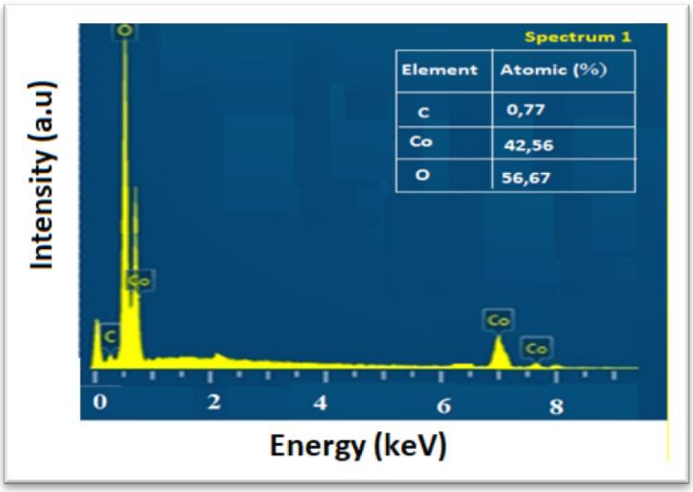

Fig 3: Energy dispersive X-ray spectrum of Co_3O_4 nanorod particles fabricated with aqueous extract of Moringa Oleifera leaves

A small amount of about 0.81% of carbon was detected. This is probably due to the vegetable material since flavonoids present in the leaves acted as capping agent to prevent the particles agglomeration. This is indicating mostly the high purity of the Co_3O_4 nanorods. The experimental atomic proportions of Co, O and C were respectively found to be 42.56%; 56.67% and 0.77%, which is closed to the theoretical stoechiometry (3:4) of Co_3O_4. The EDS spectrum supports futhermore the XRD characterization.

3.4 Analysis via Fourier transform infrared (FT- IR) spectroscopy

To investigate and confirm further the purity of the spinel oxide nanopowder prepared. FT- IR spectroscopy was carried out with objective of ascertaining the purity and nature of metal oxide spinel. The chemical bondings in the prepared material were recorded by FT- IR spectra (SHIMADZU Spectrophotometer) using KBr pellet technique. The FT- IR spectroscopy was investigated in the region: 4000 to 400 cm^{-1} and the Fourier transform infrared (FT-IR) spectrum of as synthesized Co_3O_4 nanorods is indicated in Fig 4.

The spectrum of the powder showed important absorption peaks posiotioned at about 572 cm^{-1} and at 663 cm^{-1}. The band at 663 cm^{-1} was attributed to the stretching vibration mode of O–Co–O, in which Co is Co^{2+} in tetrahedral site of the spinel. The band at 572 cm^{-1} was assigned to Co–O, where Co^{3+} occupied the octahedral site of the spinel. The absorption peaks positioned at 572 cm^{-1} and 663 cm^{-1} evidenced the presence of Co_3O_4 spinel. The appeared band at 3548 cm^{-1} could be corresponded to OH stretching of the alkaloids presente in the vegetable material a playing the role of as caping agent in the preparing Co_3O_4 and the band located at 1595 cm^{-1} has been assigned binding vibrations of absorbed water molecules on Co_3O_4 spinel [23].

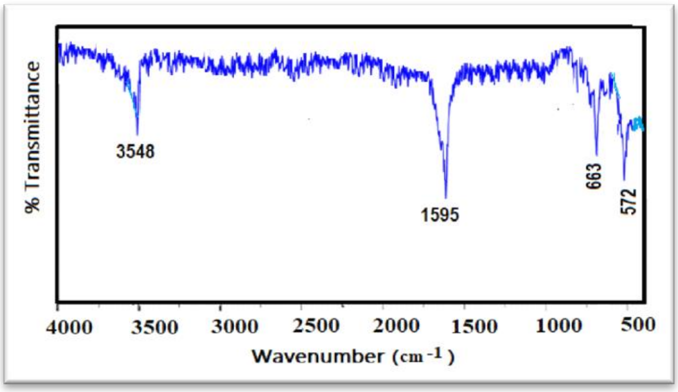

Fig 4: The FTIR spectrum of the spinel Co_3O_4 nanoparticles synthesized with aqueous extract of Moringa Oleifera leaves

3.5 Analysis via Raman spectroscopy

The composition and the structure of the isolated Co_3O_4 nanorods by using aqueous extract of Moringa Oleifera leaves was futhermore confirmed by the Raman analysis. The spectrum was taken at room temperature with a Spex1403 (laser Raman scattering spectrometer) in the range from 100 to 800 cm^{-1}. The Raman peaks in Figure 5 posiotioned about

197, 486, 520 and 691 cm^{-1} were attributed respectively to the F_{2g}^{1}, E_g, F_{2g}^{2} and A_{1g} modes of tricobalt tetraoxide (Co_3O_4) [24]. This observation is consistent with the analysis from the XRD spectrum and other analytic characterization techniques used in the present study, which furthermore confirm the synthesis of Co_3O_4.

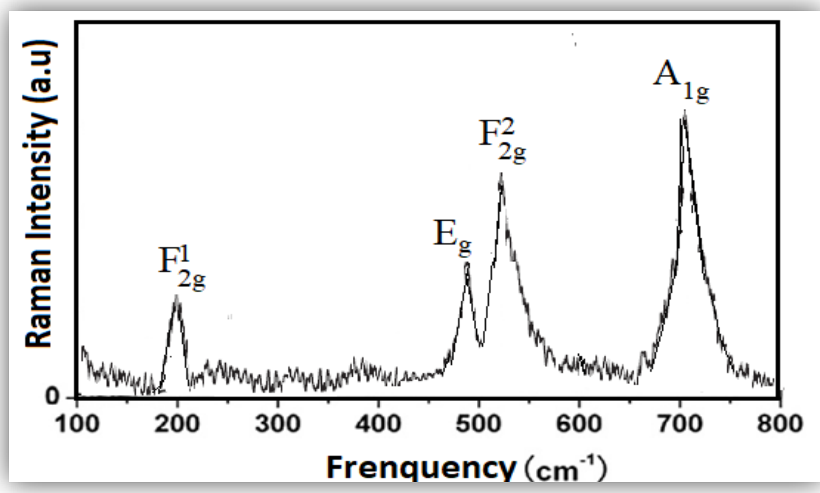

Fig 5: Raman spectrum of Co_3O_4 nanorods synthesized with aqueous extract of Moringa Oleifera leaves

3.6 Optical measurements

The UV-vis spectroscopy was used to investigate the optical absorption properties of the prepared nanorods powder. Two absorption bands were observed at wavelength ranges of about 250 nm and 530 nm. These bands may indicate ligand-metal charge transfer events. The first band can be assigned to the oxide ions (O^{2-}) to cobalt ions (Co^{2+}) charge transfer process and the second to the oxide ions to Co^{3+} charge transfer in the spinel of Co_3O_4 [25]. The optical absorption band in the visible light region, could imply the possibility of using, the prepared spinel as a photocatalyst under visible light or as a visible light emitting materials.

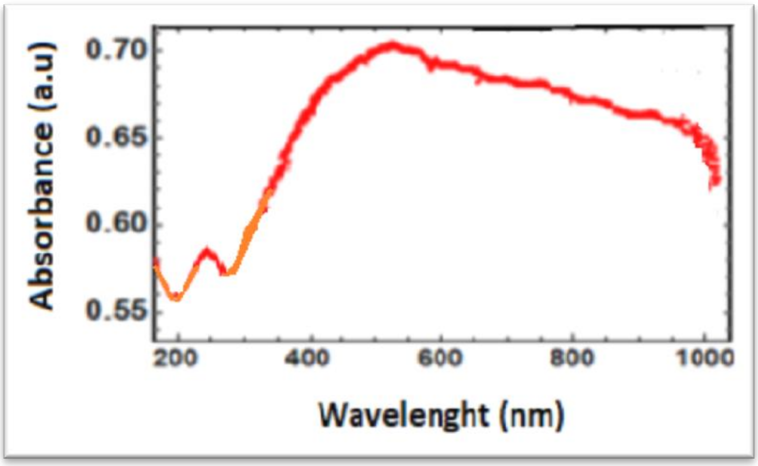

Fig 6: UV–visible spectrum of tricobalt tetraoxide nanorods fabricated with aqueous extract of Moringa Oleifera leaves

3.7 Magnetic properties

The magnetic measurements were realized at room temperature using Vibrating Sample Magnetometer (VSM). The hysteresis loop data of as prepared Co_3O_4 nanorods is shown in Figure 7. The remanent magnetization of about 0.65 emu ⁄g was measured at the maximum applied magnetic field of 12.6 kOe, indicating superparamagnetic behavior of the fabricated spinel. This spinel could consequently be used as a potential candidate in digital data applications. The adopted environmental method, employed in the present research work is expected to be applied in the fabrication of other metal oxide [26].

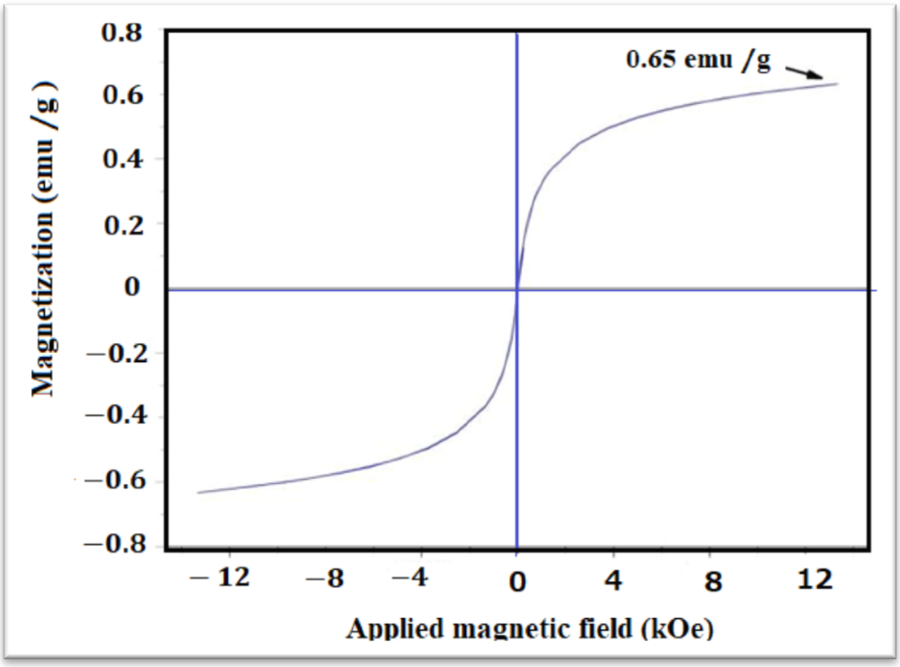

Fig 7: Magnetic hysterisis loop of tricobalt tetraoxide nanorods fabricated with aqueous extract of Moringa Oleifera leaves

4. CONCLUSION

Spinel of Co_3O_4 nanorods of about several hundred nanometers long and several tens of nanometers in diameter, have been obtained using aqueous extract of Moringa Oleifera leaves and inorganic precursor. This material was characterized by using physical and spectroscopic methods. The optical absorption spectrum of cobalt oxide exhibited a strong band in the visible light region, which implies its possibility to be used as a photocatalyst under visible light. The superparamagnetic behavior of the synthesized spinel indicated that it can be employed as a potential candidate in digital data applications.

Author Contributions: All the authors have equally contributed to this paper.

Conflicts of Interest: All the authors do not have any possible conflicts of interest.

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