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Novel greener synthesis and characterization of mixed metal oxides using cyathea nilgiriensis holttum plant extract

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Abstract

In this work we synthesized mixed metal (Zn, Mg, Cu) oxide particles via green process using cyathea nilgiriensis holttum plant extract. The presence of biomolecules and metal oxides were confirmed by FTIR. X-ray diffraction spectrum revealed that mixture of hexagonal ZnO, cubic MgO and monoclinic CuO particles were formed. Morphology of mixed oxide particles observed by scanning electron microscope suggests that most oxides particles were granular shaped. The successful synthesis of mixed zinc, magnesium and copper oxides proved the biosynthesis of the mixed oxide particles by a plant extract is an effective processing method. The fraction of MgO was found to be the highest because, MgO is one of the most stable oxides. The fraction of various oxides may be controlled by modifying the fraction of initial Zn nitrate, Mg nitrate and Cu nitrate.

Keywords: *Cyathea Nilgiriensis holttum, Mixed Oxides, Green synthesis, Morphology.*

1. Introduction

Mixed metal oxide particles possess variety of structures and characteristics [1]. Among the various oxides we selected ZnO, MgO and CuO oxide particles in order to take advantage of combination of their versatile properties. ZnO particles have been used in transparent electronics, UV resistant materials, UV lasers and LEDs [2-4]. MgO is considered as an important functional metal oxide that has been widely used in various fields, such as catalysis, refractory materials, paints, and superconductors [5].

CuO is a p-type semiconductor material with a narrow band gap of 1.2 eV. In recent years, they are receiving lot of attention for their versatile properties and potential use as gas sensors, solar cells, lithium ion batteries, heterogeneous catalysts and antibacterial agents [6-9]. The mixed metal oxides are generally prepared by co-precipitation [10], solid state chemical reaction [11], sol–gel [12] and traveling solvent-floating-zone (TSFZ) [13] methods. Due to the environmental concerns nowadays researchers focus on greener eco friendly synthesis of particles instead of physical and chemical methods. Mono metal oxide particles have been synthesized using natural extracts, but no attempt has been made to synthesize mixed oxide via green chemistry method. In this paper we synthesized successfully mixed metal oxide particles using cyathea nilgiriensis plant extract. The Mixed metal oxide (MMO) nanoparticles (also called heterometal oxide nanoparticles) can play an appreciable role in many areas of chemistry and physics and the greener biosynthesized particles particularly in the field of catalysis.

2. Materials and methods

2.1. Extraction of cyathea nilgiriensis holttum

The plants were collected from the road sides of Coonoor, Nilgiris District, Tamilnadu, India. The collected plant was authenticated in Botanical Survey of India (BSI), located in Coimbatore, Tamil Nadu, India. $Zn(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.9H_2O$ and ethanol were purchased from Merck chemicals Ltd, India and used as received without any further purification. Double distilled water was used throughout the experiment. The plant leaves of cyathea nilgiriensis were washed thoroughly with running water and subsequently incised into small pieces. It was placed in a circulating oven at 50°C until complete dryness. About 3 g of finely dried cyathea nilgiriensis holttum plant leaves were boiled with distilled water for 10 min. The extract obtained was filtered through Whatman No. 1 filter paper and the filtrate was collected in 250 mL Erlenmeyer flask and stored in refrigerator for further use.

2.2. Synthesis of mixed oxide nanoparticles

A solution containing 0.1M of $Zn(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$, $Cu(NO_3)_2.9H_2O$ was prepared in 50 mL double distilled water. Then 30 mL of cyathea nilgiriensis extract was slowly added drop wise into the solution under magnetic stirring at 80°C for about 4 h to obtain a complex. The complex formed after adequate time of stirring was collected by centrifugation at 5000 rpm for 10 min. The separated complex was dried in an oven at 40 °C for 8 h and then calcined in muffle furnace at 450 °C to get mixed metal oxide nanoparticles.

2.3. Characterization

To confirm the functional bio-molecules associated with the mixed oxide particles, FTIR analysis was carried out using Nicolet 520P FTIR spectrometer in the range of 500-4000 cm^{-1}. The purity of the synthesized mixed oxide was confirmed by XRD analysis. It was carried out using Cu Kα radiation (K=1.5418 A^o) on a JEOL JP x 8030 X-ray diffractometer. The surface morphology of the product was recorded using scanning electron microscopy (S-3000H; Hitachi, Japan). Elemental analysis and energy-dispersive X-ray spectroscopy were performed to evaluate the composition of the sample along with the scanning electron microscopy observation.

3. Results and discussions

3.1. FTIR analysis

Fig. 1 represents the FT-IR spectrum of bio synthesized mixed oxide particles using cyathea nilgiriensis plant extract. FTIR measurements were used to identify the biomolecules for capping and proficient stabilization of the metal particles synthesized by cyathea nilgiriensis plant extract. Absorption peak in the range 530-560 cm^{-1} in the FTIR spectra confirms the formation of mixed metal oxide particles. The O-H stretch appeared as a very broad band extending from 3573 cm^{-1}. This very broad O-H stretch band is seen along with a C=O peak, suggesting that the compound is an aliphatic carboxylic acid. Medium absorption in the region 1590-1468 cm^{-1} implies the presence of aromatic ring. The absorption peak at 1047 cm^{-1} corresponds to C-O stretching of saturated primary alcohol. The prominent doublet absorption at 2934 cm^{-1} indicates C-H stretching vibration of an aromatic aldehyde. The band at 1688 cm^{-1} corresponds to the carbonyl group of flavonoids.

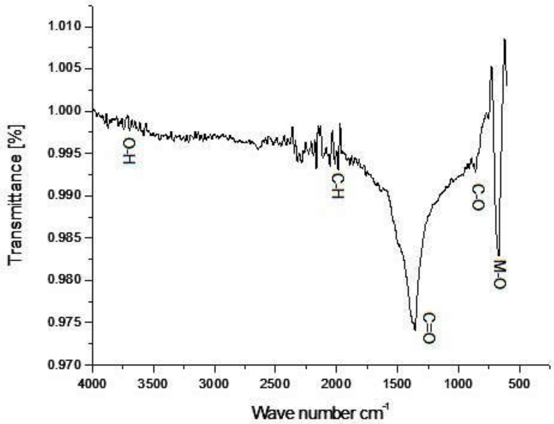

Fig. 1. *FTIR spectrum of mixed oxide particles*

The results of FTIR analysis confirmed that phenolic compounds in flavonoids have a stronger tendency to bind with metal, indicating that phenolic group could possibly form metal nanoparticles to prevent agglomeration and thereby stabilize the medium. Biological molecules could possibly perform dual functions of formation and stabilization of oxide particles in aqueous medium. The additional peaks represent some impurities in the plant extract. The following equation describes the formation mechanism of metal oxide nanoparticles when the phenolic group present in the plant extract reacts with metal nitrate to form metal hydroxide particles. The metal oxide particles are produced during the subsequent calcinations process.

$$2M{-}(NO)_3 + 2OH^- \rightarrow 2M{-}(OH)_2 + 2NO_2 + O_2$$

$$2M{-}(OH)_2 \rightarrow 2MO + 2H_2O$$

Where M = Zn, Mg, Cu

3.2. XRD studies

Fig. 2 shows the XRD spectrum of the biosynthesized mixed oxide particles. The XRD pattern shows three different sets of peaks for ZnO, MgO and CuO. The major peaks for ZnO (Zincite) particles correspond to Bragg reflections with 2θ values of 31.74°, 34.44° 36.23°, 47.53°, 56.60°, 62.81°, 68.01°, and 69.01°. These location of the characteristic Bragg reflections were indexed to (100), (002), (101), (102), (110), (103), (112) and (201) planes of ZnO hexagonal structure, respectively, (standard JCPDS card 79-2205) and this confirmed the presence of zinc oxide particles. Similar type XRD patterns were obtained in green synthesis of ocimum basilicum L. leaf extract [14].

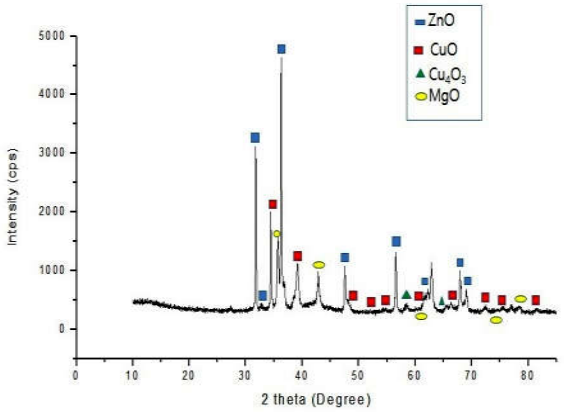

Fig. 2. *XRD spectrum of mixed oxide particles*

The major peaks for MgO (Periclase) particles correspond to Bragg reflections with 2θ values of 36.54°, 42.84°, 61.88°, 74.50°, and 78.45° and their characteristic location indexed as (111), (200), (220), (311) and (222) planes of MgO cubic phase structure with standard (JCPDS card 01-073-38185) and this confirmed the presence of MgO particles. The periclase type MgO particles were observed in Artemisia abrotanum herba extract [15]. The Bragg reflections major peaks for CuO (Tenorite) particles correspond to the 2θ values as 35.76°, 39.09°, 49.68°, 53.24°, 50.20°, 61.40°, 66.12°, 68.24°, 72.30°, 75.48° and 82.30° and corresponding Bragg reflections were indexed as (111), (200), (202), (020), (202), (113), (311), (220), (311), (222) and (313) planes of CuO monoclinic structure (JCPDS card 01-1117). Similarly, the Bragg reflections major peaks for Cu_4O_3 (Paramelaconite) particles correspond to the 2θ values as 36.22°, 42.85°, 58.35°, 64.07° and 65.19° and their characteristic location indexed as (004), (220), (224), (400), (206) and (422) planes of Cu_4O_3 tetragonal structure (JCPDS card 49-1830). The excellent agreement between the observed peaks and the standard confirms the presence of CuO particles. It should be noted that formation of complex oxides or the reaction between three oxides were not observed in the present study.

3.3. SEM-EDX analysis

Fig. 3. (a-f) shows the SEM, elemental mapping and EDAX spectra of synthesized mixed metal oxide nanoparticles. The particles appear agglomerated and some of the individual granules are clearly visible. Fig.3. (b-e) shows the elemental mapping analysis images of mixed oxides. The presence of metals (Zn, Mg, Cu) and oxygen in the elemental mapping images (Fig. 3) and the absence of XRD peaks from metallic elements in Fig. 2. strongly suggests that these particles are not elemental metals but oxides. Further, Fig. 3(f), the EDAX image confirms the occurrence of the zinc, magnesium and copper particles in its oxide form, supporting the biosynthesis of the mixed oxide particles is an effective processing.

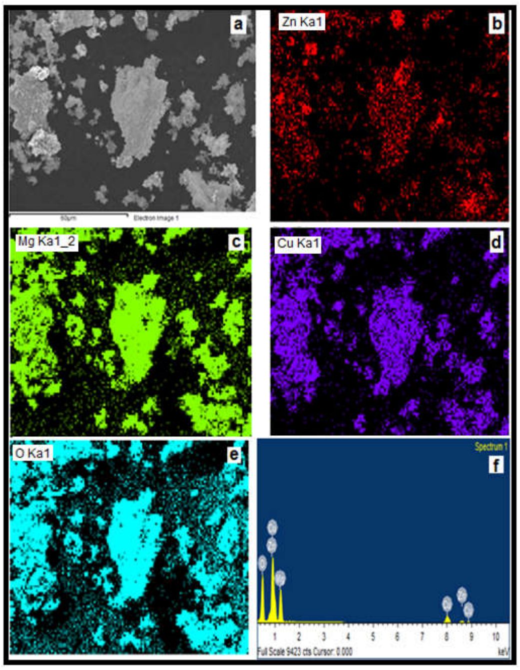

Fig. 3. *(a) SEM, (b-e)) Elemental mapping and (f) EDX spectrum of mixed oxides*

The elemental composition of mixed oxides shows that the fraction of MgO was found to be highest because MgO is one of the most stable oxides. The fraction of various oxides may be controlled by modifying the fraction of initial Zn nitrate, Mg nitrate and Cu nitrate.

4. Conclusions

We adopted the eco friendly green process to synthesize renewable and low cost mixed oxide particles using cyathea nilgiriensis holttum plant extract for biomaterial applications. Through FTIR studies we found the presence of phenolic group of flavonoid acts as capping molecule and involved in formation of metal oxide. The crystalline phases of hexagonal ZnO, cubic MgO and monoclinic CuO were confirmed by XRD analyses. The synthesized mixed oxides are expected to have widespread applications in various industries because of their multi-functional properties. This method may be extended to synthesize different mixed metal oxide particles.

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