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Biosynthesis of Manganese oxide nanoparticle using *Murraya Koenigii*

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Abstract

The rise of nanotechnology has brought to the world a new potential and the use of different nanomaterials has revolutionized both the industrial and biomedical worlds with the broader perspective of what humanity can achieve through material manipulation at the nanoscale. Nanoscale particles possess distinct characteristics which advances in exploring and exploiting the uses of nanostructured materials. Due to the high surface to volume ratio and high reactivity there is a great potential for metal and metaloxide nanostructures. Synthesis of nanoparticles by physical and chemical methods are costly and toxic to the environment. Use of biosynthesis provides advancement over physical and chemical methods and may lead to the development of clean, non-toxic and environmental acceptable procedures which involves organisms ranging from bacteria to fungi and also plants. Green synthesis of metal nanoparticles is an expanding area of research and in the current study, *Murraya koenigii* i.e., Curry leaf powder was used for the green method by which manganese oxide nanoparticle synthesis was developed. *Murraya Koenigii* which belongs to Rutaceae family has found to be potent antioxidant due to high concentrations of carbazoles, a water soluble heterocyclic compound and also responsible for the reduction of metal ions. The present study focus on the development manganese oxide nanoparticles from the leaf extract of *murraya koenigii* where potassium permanganate act as precursor. Crystal phase identification of manganese oxide nanoparticles was studied by X-ray diffraction analysis and optical characterisation was carried out using Uv-Vis spectrophotometer.

Keywords: Biosynthesis, *Murraya Koenigii*, Uv-Vis, X-ray diffraction.

1. Introduction

Nanotechnology is an interdisciplinary field of research combining biology, chemistry, physics and material science which involves working with particle of sizes upto 100 nm [1]. Over the past decade the synthesis of metallic nanoparticles has accrued utmost interest owing to their fundamental scientific significance and also due to the potential application that derive from the fascinating electrical, magnetic and catalytic properties that make them applicable in different

fields of science and technology [2]. Materials in nanometer regime display exclusive physicochemical attributes contrasted with their bulk materials [3]. It is known that the phases, sizes and morphologies of nanomaterials have great influence on the properties and applications, therefore many research efforts have focussed on rationale control of phase, shape, size and dimensionality of nano materials [4]. Notable improvements have recently been accomplished in the field of nanoparticles synthesis from different materials and lots of effort has been done to

control their size, composition and uniformity. Nano particles have characteristic physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties in each spatial dimension which are usually 0.1 to 100 nm in size. There is a considerable keen on obtaining well diffused, ultrafine and monotonous nanoscale to delineate and take their distinct distinguished [5]. Certain reactive functional groups bear chemically synthesised nanoparticles, which can be harmful to the biological system. So the biosynthesis of nanoparticles using plant and micro organism has emerged as an interesting area which is also an emerging highlight with the intersection of nanotechnology and biotechnology and has become a really good alternative for the obtention of safer and more benign products not only for the environment but also for the people who potentially will use them [6]. Biomolecules present in plant extracts can be used to reduce metal ions to nanoparticles in a single step green synthesis process. The use of plant extracts mainly concerns with the elimination of hazardous wastes and implementation of environmental friendly solvents for making metallic nanoparticles and is an inexpensive, easily scaled up process. This sort of green synthesis involve the use of different biological systems like bacteria [7], yeast [8], fungi [9], algae [10] and plants [11]. Among the available green method for synthesis of metal/metaloxide nanoparticles utilisation of plant extracts offer several advantages and is a simple, rapid, cost effective method which is also suitable for large scale synthesis of nanoparticles. Researchers have reviewed that biomolecules present in plant extracts like alkanoids, terpenoids, flavonoids, sugars and aminoacids can act as reducing and stabilising agents in the biosynthesis of nanoparticles [12].

Because of its variant catalytic and adsorption properties, the manganese oxide nanoparticles have recently been in focus. Many structural types have been obtained depending on the preparation of manganese oxide particles and each of these differs in their crystalline structure, morphology and dimensions, leading to diversity in their applications. Normally, it has wide applications in catalysis, ion exchange, molecular

adsorption, solar energy transformation, varistors, high-density magnetic storage media, electrochemical materials, biosensor, and particularly energy storage. Intensive researches have been done on Manganese oxide nanoparticles leads to the discovery of their applicability in a variety of fields such as protein immobilisation [13], removal of dyes [14], lithium-ion batteries [15], synthesis of bio-active compounds [16], and analysis of neuro-behaviour of rats [17]. In the current research, an approach to manganese oxide nanoparticle has been formulated by synthesis utilising *Murraya koenigii* i.e., Curry leaf, powder as a green mechanism. *Murraya Koenigii* (Curry leaves) belongs to *Rutaceae* family has recently been found to be potent antioxidant due to high concentrations of carbazoles, a water soluble heterocyclic compound [18] which is responsible for the reduction and stabilization of metal ions. Curry leaves are well known as spice but has also been used in traditional medicine as a treatment for variety of ailments. When curry leaf powder is added to the diluted potassium permanganate solution, it results in the reduction of manganese oxide nanoparticles. The resulting nanoparticles are characterized through X-ray diffraction (XRD) and UV-visible spectroscopy.

2. Experimental procedure

The collected fresh leaves of *Murraya koenigii* were washed thoroughly with deionized water to remove any dirt particles. The washed leaves were then air-dried. The cleaned and dried leaves were ground into powder and the prepared powder was used for preparing the samples. The samples were prepared at different molarities. For each molarity, the calculated amount of KMnO_4 purchased from Sigma Aldrich was taken and dissolved in distilled water and stirred for few minutes. At the time of stirring, curry leaf powder was added pinch by pinch to the solution. The mixture was constantly stirred for 2 hours for the proper reduction of metal ions. It results in the colour change and the dark purple colour changed to brown colour, which indicates the formation of nanoparticles. The same procedure is repeated for preparing all the other samples.

3. Results and discussion

The crystal structure and phase purity of

the samples were analysed using X-ray diffractometer. The characterisation is significant as it helps in understanding the size, shape and morphology of the synthesised nano particles. The optical studies were carried out by UV-Vis spectrophotometer.

3.1 Structural characterisation

X-ray diffraction data were recorded and collected by the XRD model X'Pert Pro Powder X'Celerator Diffractometer using CuK_α as characteristic radiation ($\lambda=0.15418$ nm). The accelerating voltage was 40kV and emission current were 30mA respectively. The measurements were made in 2θ range from 20° to 80° with a scan rate of $3^\circ/\text{min}$. The XRD patterns of the prepared nanoparticles were analysed and the results are presented.

According to the results obtained the unannealed samples showed no peak indicating that the prepared nanoparticles were not crystalline in nature. Therefore the samples were annealed at 400°C for about an hour in a Muffle furnace. On

annealing the samples the crystallinity gets increased which can be seen from the variation of intensity in the peaks. All the diffraction peaks were readily indexed to Mn_3O_4 with tetragonal structure (JCPDS – 89-4837). Thus the annealing process leads to polycrystalline nature of particles with tetragonal geometry. Distinct peaks of (112), (200), (103), (211) and (215) corresponds to the crystal planes and these orientations clearly reveals that the prepared particles are polycrystalline in nature. The Mn_3O_4 lattice constants obtained by refinement of the XRD data of the nanoparticles are $a = 5.778 \text{ \AA}$ and $c = 9.0355 \text{ \AA}$ which are consistent with the standard values and have been determined from interplanar spacing of different (hkl) planes. The calculated unit cell parameter for tetragonal structure were found to be in good agreement with the referred values (JCPDS 89-4837). The slight variation in lattice parameter may be due to the stress developed in the formation of particle.

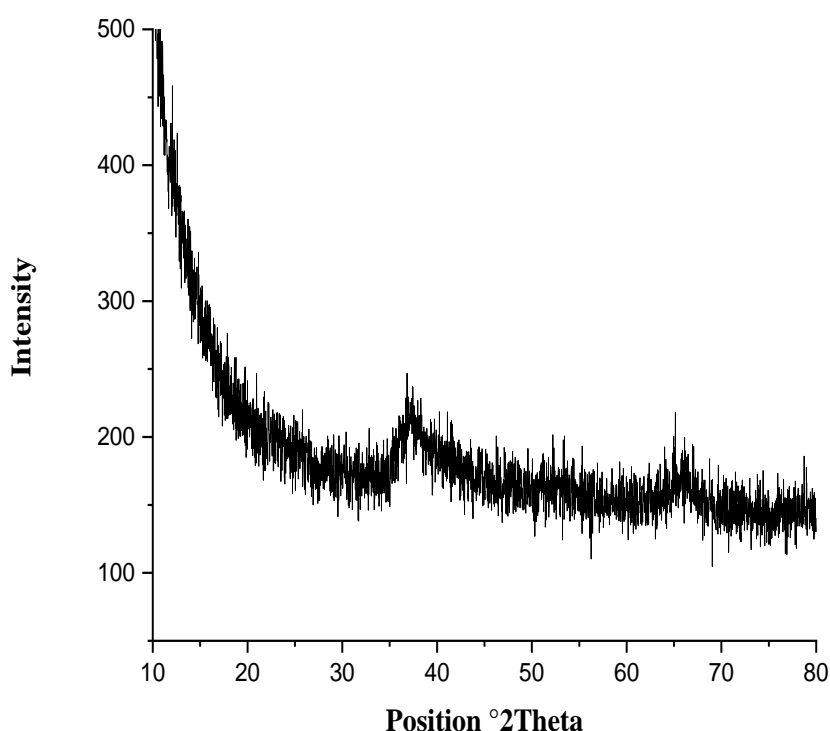


Fig.1. XRD pattern for unannealed sample1

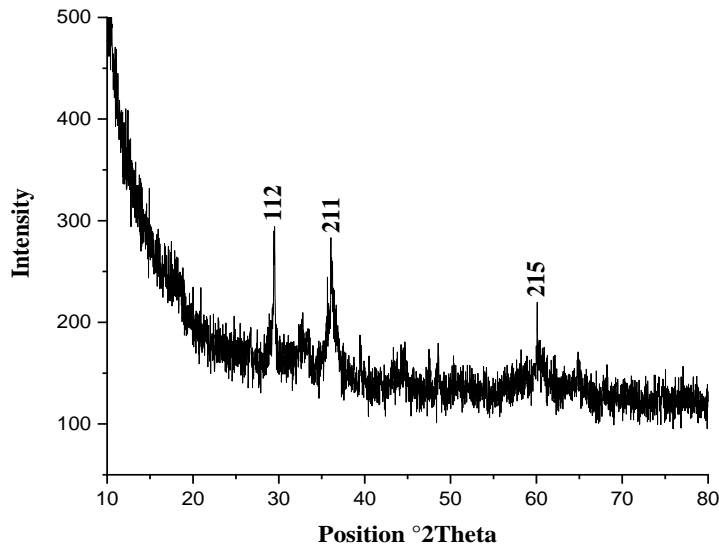


Fig.2. XRD pattern for annealed sample 1

The crystallite size is evaluated from the FWHM of the plane using the Debye Scherrer’s equation,

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where D is the average crystallite size of the

prepared nanoparticles, k is the Debye–Scherrer constant (0.9), λ is the wavelength of incident X-ray radiation (0.154 nm), β is the width of the peak with the maximum intensity in half height in radian and θ is the Bragg’s diffraction angle. The average crystallite size calculated for the different samples was found to be in the range of 32 nm to 50 nm.

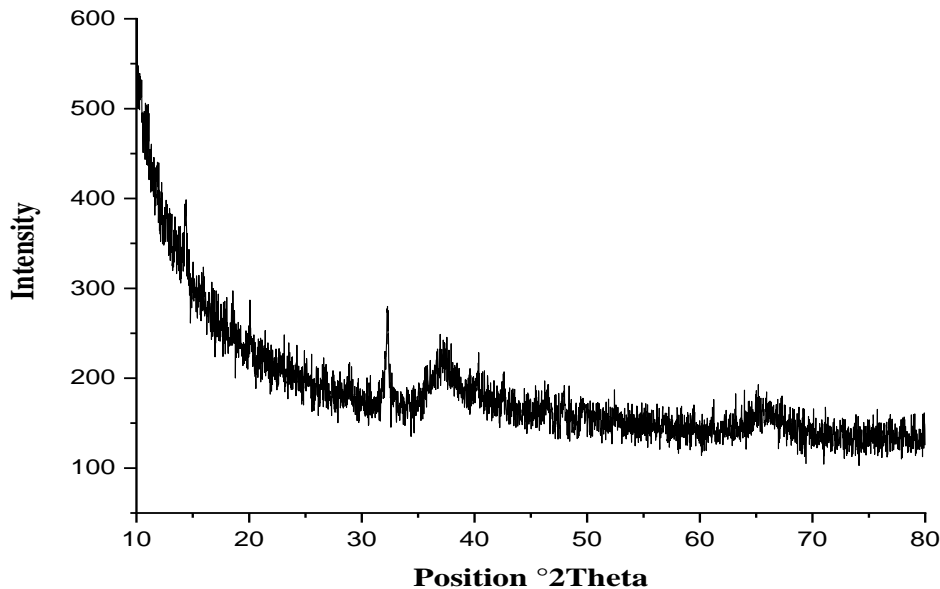


Fig.3. XRD pattern for unannealed sample 2

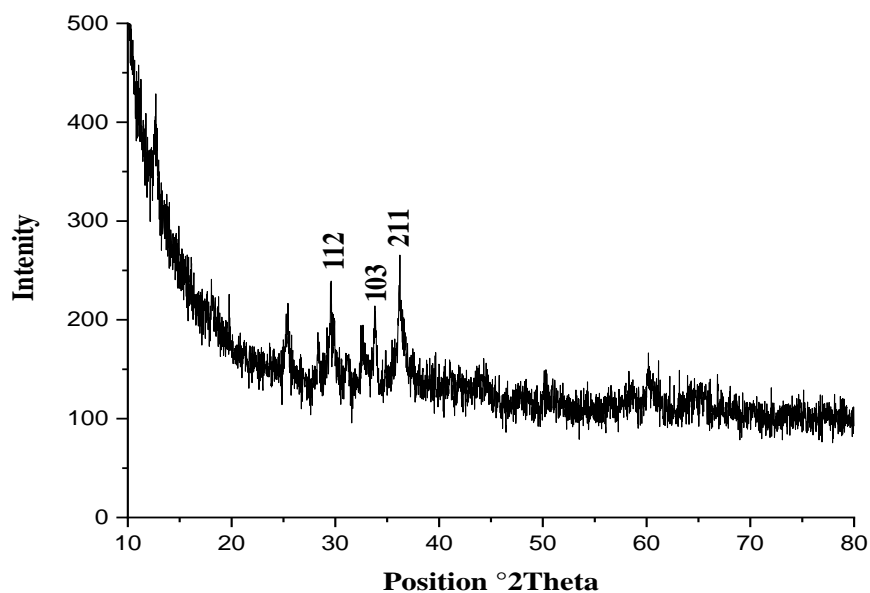


Fig.4.XRD pattern for annealed sample 2

The micro strain (ϵ) of the prepared samples is calculated using the relation,

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (2)$$

Thus the micro strain for the samples were found to be around 6.657×10^{-4} to 8.327×10^{-4} .

3.2.Optical characterisation

The optical behaviour and properties of the prepared nanoparticles were studied using UV-Visible spectrophotometer. Figure 5 & 6 displays UV-Vis absorption spectra of synthesised Mn_3O_4 nanoparticles.

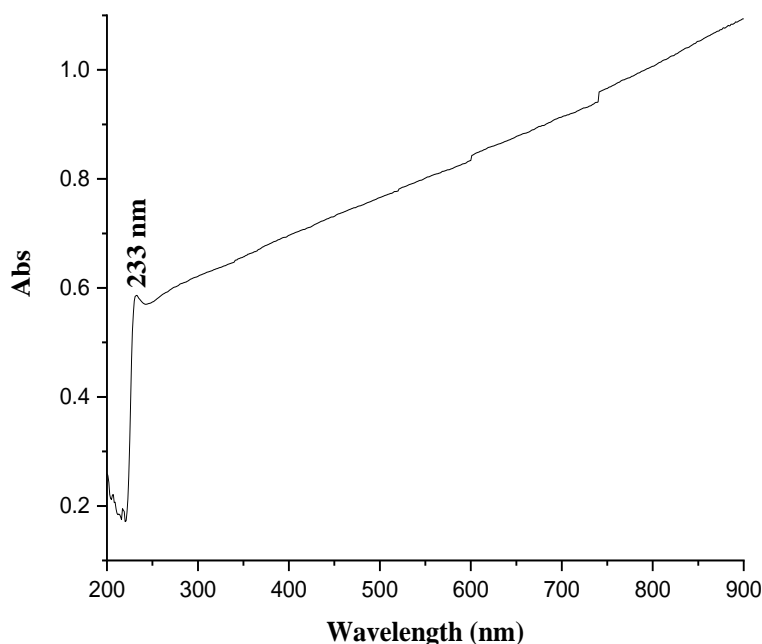


Fig.5. UV-Vis absorption spectra of annealed sample 1

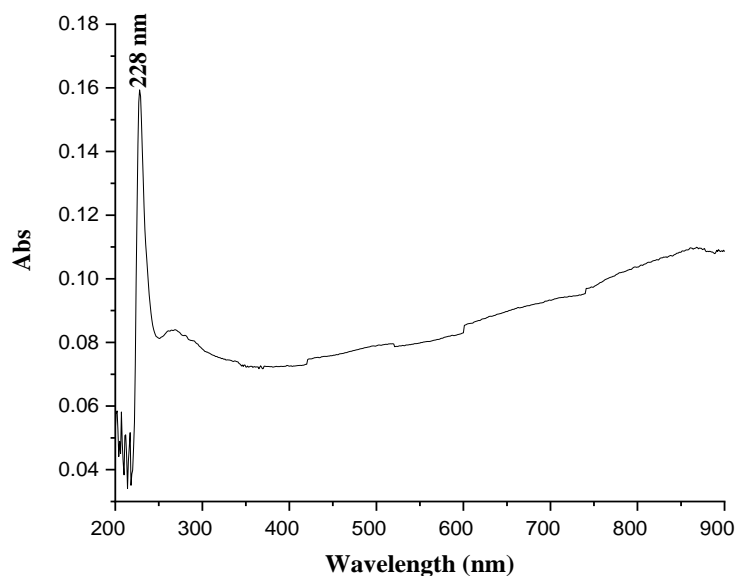


Fig.6. UV-Vis absorption spectra of annealed sample 2

The absorption spectra exhibit an intense absorption band around 233nm and 228 nm. The corresponding bandgaps were calculated and the absorbance peak was found to be blue shifted compared with bulk values and it revealed the quantum confinement. The optical absorption in the wavelength shorter than 400nm region is mainly attributed to the electron transition from the top of the valence band to the bottom of the conduction band [19].

Conclusions

The key purpose of the current work was to synthesis manganese oxide nano particle with the technique which stands economic both in costs and time. The proposed biosynthesis method is a simple and better method for the synthesis of metal oxide nanoparticles and manganese oxide nanoparticles have been successfully synthesised. Structural and optical characterisation was carried out using X-ray diffractometer and UV-Vis spectrophotometer. The structure of nano particles, cell parameters and strain were calculated from XRD results. The results revealed a tetragonal structure and the lattice parameters calculated from XRD pattern are well supportive with the standard reported values. Using Scherrer's formula the average crystallite size was also calculated. The UV-Vis spectral analysis revealed that the sample had good absorbance and the bandgap calculated

were found to be blue shifted than bulk values which revealed quantum confinement in manganese oxide nanomaterials.

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