Synthesis and Investigations on structural, optical, thermal and electrical conductivity of α-MnO_2 nanoparticles

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Abstract

Microwave assisted solution method have been used to synthesis α-MnO_2 nanoparticles. The prepared sample was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Thermo gravimetric Differential thermal analysis (TG-DTA) and AC impedance spectroscopy. From the XRD analysis of the prepared MnO_2 nanoparticles size which was around 35 nm. From the HRTEM image also we obtain the average particle size was around 35 nm. FTIR revealed the chemical composition and interaction of functional groups of MnO_2 nanoparticles. SEM image shows the aggregates are mostly particles with random shapes. From the optical study we report the energy band gap value as 2.69 eV and it was found that the particle. The conductivity of prepared nanoparticles has been in the order of 10^{-7} S cm^{-1}.

Keywords: MnO_2, Microwave method, XRD, SEM, HRTEM.

Introduction

Among metal oxides MnO_2 shows a great potential as an alternative material because it is economical. It is available in abundance and is environment friendly. Manganese oxides have long been known as materials of technological importance for catalytic and electro chemical applications. Various methods have been reported to synthesize such materials, including hydrothermal reaction [1], thermal decomposition [2], electro deposition [3 ,4],template method [5] and micro emulsion method[6, 7]. There are several different crystallographic form of MnO_2, such as α, β, γ, δ, and ε- type. Manganese dioxides have attracted a great deal of interest due to their distinctive physico chemical properties and potential applications in the fields such as catalysts [8], ion exchangers [9], magnetic materials [10] alkaline batteries [11] and super capacitors[12].Microwave heating has been introduced to assist synthesis of MnO_2 materials recently. For example Nqutu et al. prepared α MnO_2 nanofibres in mixed with aqueous and Dimethyl sulfoxide solvent by use of microwave reflux [13]. This process required about 10 min to start crystallizing α MnO_2 phase and about 90 min to fully crystallize the phase. Huang et al. used a microwave hydrothermal technique to prepare α MnO_2 nanofiber at 200ºC with a hold time of 10s to 30 min [14]. Ming et al reported the synthesis of δ MnO_2 nanospheres by hydrothermal method at 75ºC in 30 min. However a facile process to synthesize MnO_2 with different crystal structures and morphologies is still a challenge by the microwave assisted method. Different methods are used to synthesize metal oxide nanoparticles.

But microwave assisted solution method have environmental approach. Microwaves are the electromagnetic radiations with wavelength ranging from 1mm to 1m in free space and frequencies between 300GHz to 300 MHz respectively. The most common microwave frequency used for carrying out the research work is 2.45 GHz, similar to the frequency of domestic microwave oven. By the use of microwaves the synthesis of inorganic compounds has gained great importance, because this method offers several advantages compared to conventional heating method. Such as rapid heating, energy saving, fine micro structure, better product quality, environment friendliness etc. Microwave assisted synthesis is cleaner, faster and economical than the conventional method. So MnO_2 nanoparticle has been synthesized via microwave assisted solution method at short time (9 min). The crystalline nature, chemical composition, Morphology and optical studies were discussed in this work.

Materials and methods

Manganese II sulphate, manganese oxalate and NaOH were procured with analytical grade. In a typical synthesis by using manganese salts of two different anions which are manganese II sulphate and manganese oxalate. Both salts of equal concentration ie 0.25 M are mixed with continuous stirring at room temperature. While stirring NaOH solution was added till the PH value of solution become 12. The stirring was continued for 1 hour again at room temperature. Then the solution becomes brown in colour. Again the solution was transferred to house hold microwave oven to irradiate the mixer for 9 min. Later than cooling to room temperature the products were collected and washed several time with deionized water and ethanol in order to remove impurities and then dried at 70ºc for 5h under air atmosphere.

Result and discussion

X-ray diffraction pattern were obtained using X pert pro system with CuKα radiation the particle size was calculated using Scherer equation. The average particle size was around 35 nm.

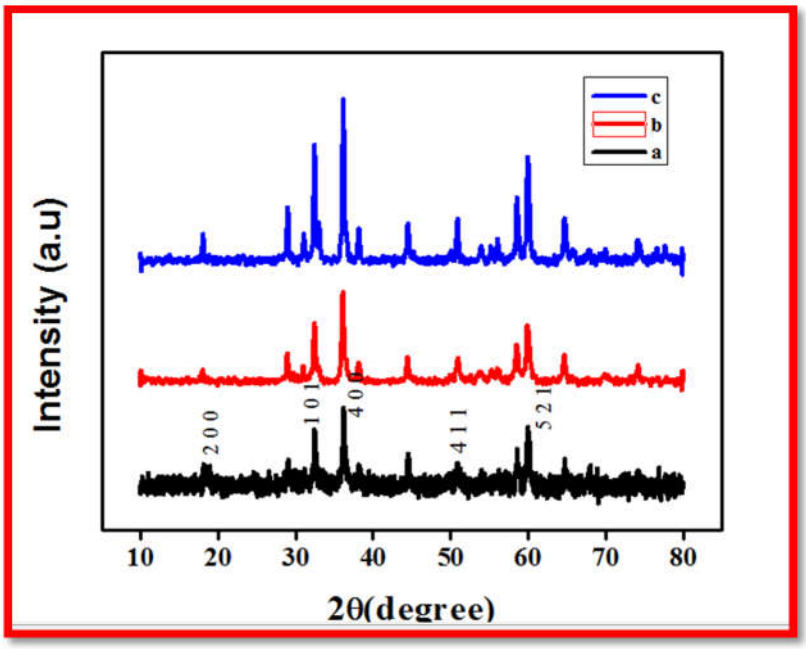

Fig 1: XRD pattern for (a) MnO_2 (b) Calcinated at 200ºC (c) 500ºC

Fig 1 shows the XRD pattern of the prepared α MnO_2 nanoparticles calcinated at (b) 200ºC (c) 500ºC .Obviously all the peaks in fig correspond to (JCPDS data no 72-1982) tetragonal system having the significant peaks at 36.2º , 32.2º , 59.9º which can be indexed h k l values at (4 0 0) (1 0 0) (2 6 0). Good crystalline structure has been evidenced by strong diffraction peaks. The resulting product was subjected to heat treatment at temperatures 200ºC and 500ºC. Compared as prepared samples the calcinated samples peak intensity has been increased but peaks position did not be changed. This shows the sample can't decompose before 500ºC.

The morphology of the product was investigated by SEM. **Fig (2)** shows a typical SEM image with panoramic view of the resulting product. The sample mainly consists of aggregates of random shapes with size varying from hundreds of nanometer to few micrometer, this indicates that the MnO_2 nanoparticles exhibit the agglomeration occurred during the synthesis due to the presence of Van der walls force.

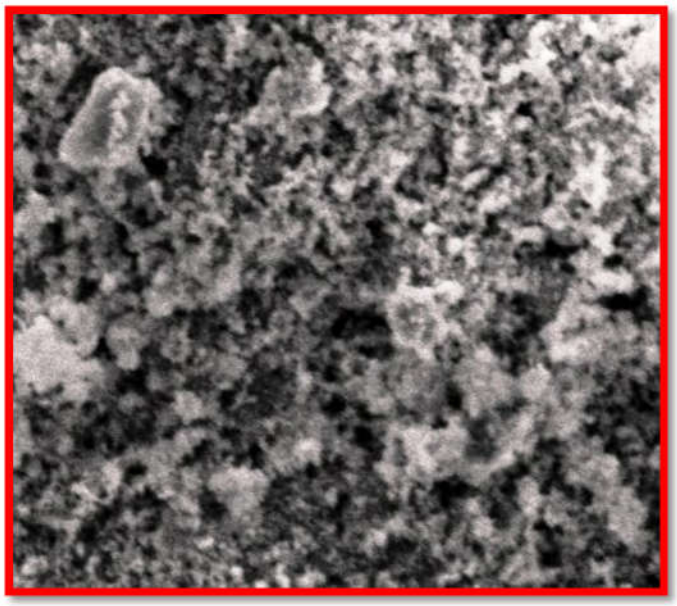

Fig 2: SEM image of MnO_2 nanoparticle.

Fig (3) shows high resolution TEM image of the prepared sample. It was found that the product consists of particles with different sizes and shapes indicating the formation of aggrigates. The average particle size of MnO_2 nanoparticle has been found around 35 nm. From the high magnifications of TEM image the clear lattice fringes were observed, this indicates the crystallinity of the sample. SEAD pattern shows the diffraction ring spot corresponds to phase selection with crystallinity. So similar results obtained from XRD also.

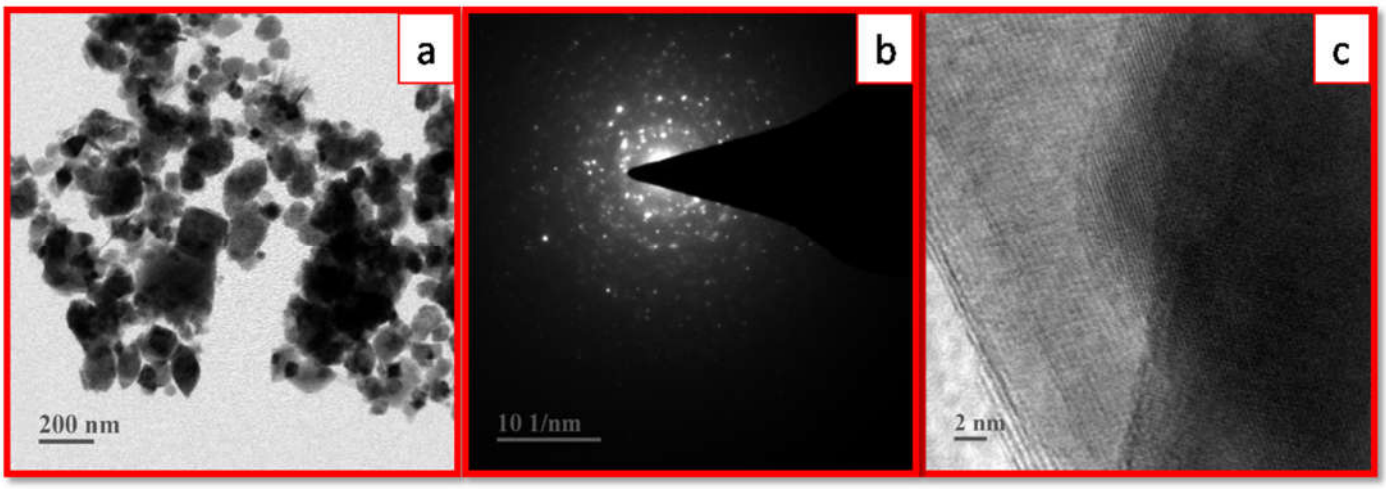

Fig 3: HRTEM image of MnO_2 nanoparticle.

Structural information of the synthesized MnO_2 nanoparticle was obtained by Fourier transform infrared spectroscopy (FTIR). The formation of MnO_2 and organic residue on the surface of MnO_2 nanoparticle was analyzed. **Fig 4** shows the two strong peaks 494 cm^{-1} and 604 cm^{-1} arising from the stretching vibration of Mn-O and Mn-O-Mn bonds indicating the formation of MnO_2 nanoparticle. The absorption peak at 1112 cm^{-1} corresponds to the C-OH stretching and OH bending vibrations. Where the bonds at 1385 cm^{-1} 1580 cm^{-1} and 1636 cm^{-1} corresponds to C-OC hydroxyl stretching and O-H bending vibration. These results indicate that some organic residues such as hydroxyl and carboxyl groups present on the surface of the MnO_2 nanoparticles. The FTIR analysis presented here is consistent with the results reported in the literatures [15, 16]

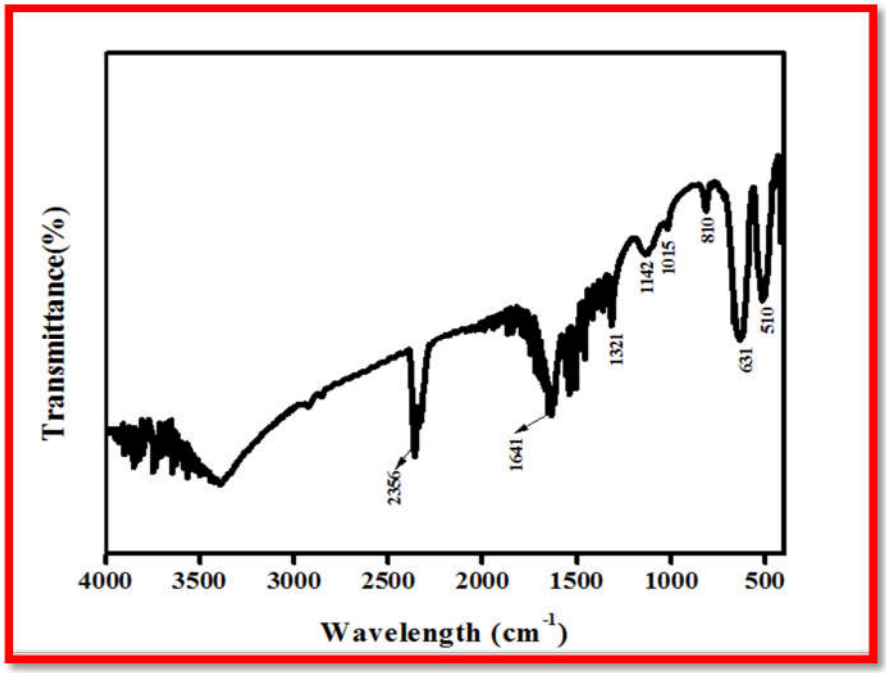

Fig 4: FTIR spectrum of MnO_2 nanoparticle

Fig **5** shows the UV DRS spectrum of the prepared MnO_2 nanoparticle The optical band gap energy for the prepared sample was determined from diffuse reflectance spectra using Kubelka-Munk equation:

$$(F(R_\infty).h\gamma^2) = A(h\gamma - E_g)$$

where $F(R_\infty)$ is the reemission parameter or Kubelka- Munk function, $h\gamma$ is the incident photon energy,R_∞ is the diffuse reflectance that is obtained from $R_\infty = R_{sample}/R_{standard}$, and A is a constant depending on the transition probability and the diffuse reflectance R_∞[14].The values of $(F(R_\infty).h\gamma^2)$ versus $h\gamma$ was plotted for the prepared sample as shown in Figure 6. Straight line was drawn to fit the experimental curve and was extended to cut off the $h\gamma$ axis in order to determine the optical band gap value of the MnO_2 nanoparticles. It was found that the optical band gap of prepared MnO_2 nanoparticle has been 2.69 eV.

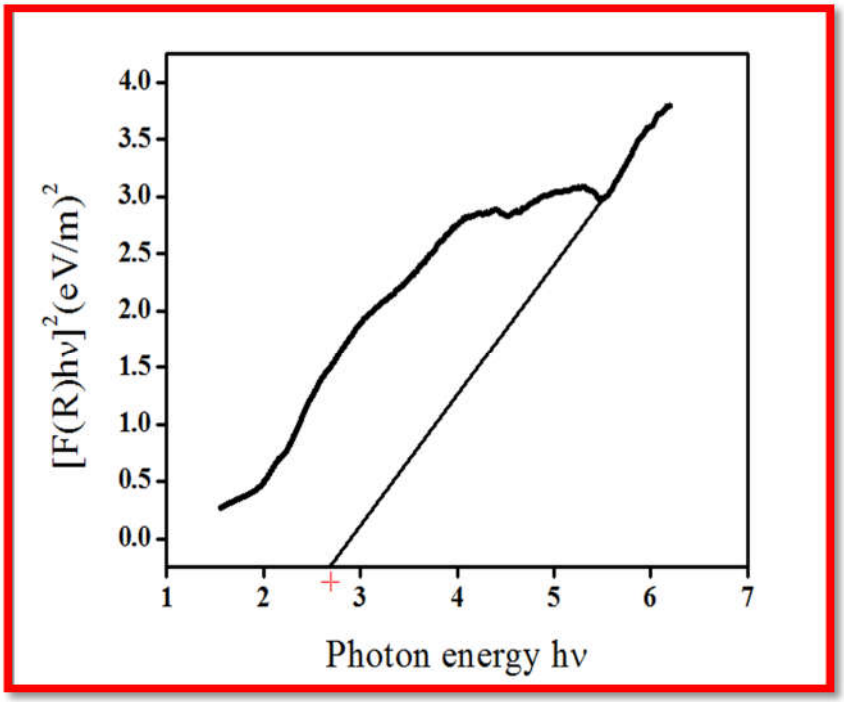

Fig 5 : Optical band gap of MnO_2 nanoparticle using Kubelka-Munk function

The TG study is important to check the thermal stability of a substance. The TG of MnO_2 nanoparticle was carried out using Thermal analyzer in air atmosphere at a heating rate of 20ºc per minute for a temperature range of 20ºC- 1000ºC **Fig (6)** shows the typical TG behavior of the synthesized MnO_2 nanoparticle. A mass loss of 16% at temperature higher than 600°C has been detected. The apparent mass loss about 9% from room temperature to 200°C can be assigned to the loss of absorbed water and crystalline water. The synthesis MnO_2 decomposes after 600°C. This result also supported by XRD analysis. **Fig 1** shows XRD pattern of MnO_2 nanoparticle being annealed at 200°C and 500°C for 2 hrs. The peaks indicates that in pure MnO_2 nanoparticle , but the intensity of diffraction peaks increases which indicates that the MnO_2 does not decomposes at a temperature 500°C or below .This is in good agreement with TG - DTA result.

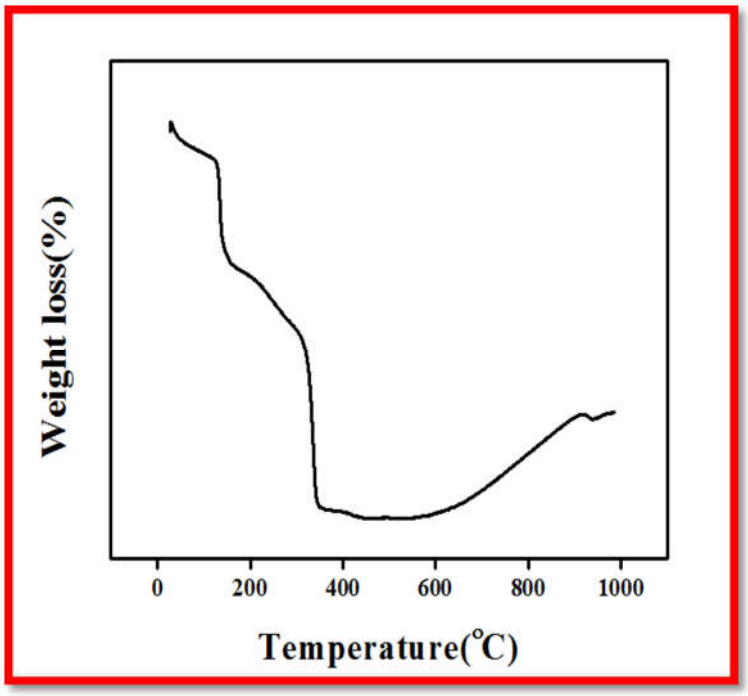

Fig 6 : TG spectrum of MnO_2 nanoparticle

The dielectric behavior may be described by the real and imaginary parts of the complex permittivity, ε^* which is defined by the relation

$$\varepsilon^* = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$$

Where real $\varepsilon'(\omega)$ and imaginary $\varepsilon''(\omega)$ are the storage and loss of energy in each cycle of the applied electric field respectively. **Fig 7(a)** and 7**(b)** shows the frequency dependence of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for MnO_2 nanoparticle. It is clear from the value of $\varepsilon'(\omega)$ are very high at low frequency and decrease with increase of frequency and become constant at high frequencies. Such high value of dielectric permittivity at low frequencies has been explained by the presence of space charge effects, which is due to the accumulation of charge carriers. Both $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ decrease with the increase in frequency. The large value of dielectric constant at lower frequency was attributed to the predominance of species like Mn ions, oxygen vacancies .The decrease in dielectric constant with increase in frequency is natural because of the fact that any species contributing to polarizability.

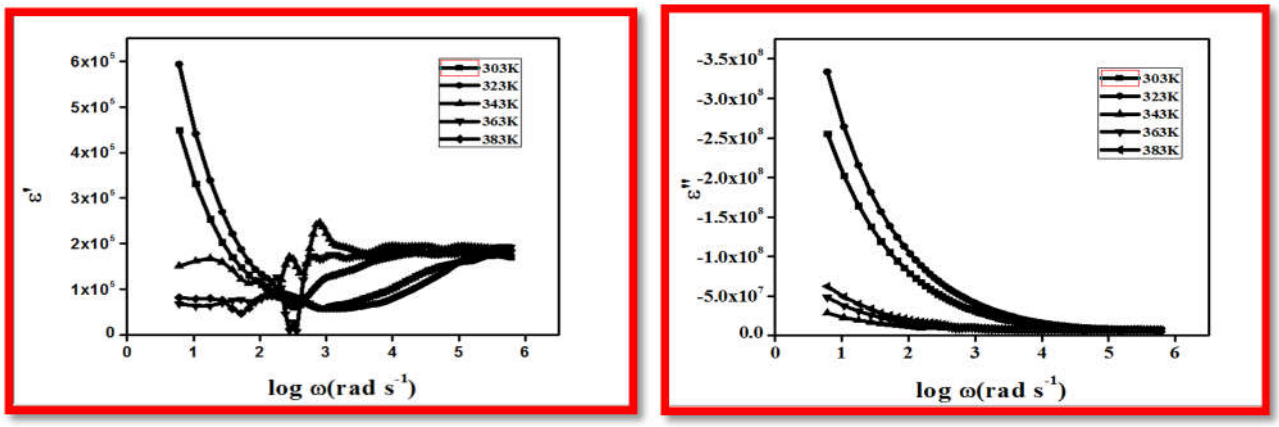

Fig 7: Frequency dependence of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for MnO_2 nanoparticle for various temperature

Conclusion

MnO_2 nanoparticles were prepared successfully by using manganese II sulphate and manganese oxalate salts. The synthesized MnO_2 nanoparticles have large specific surface area with random shapes. The simple cost effective and environment friendly approach can be scaled up to large quantity of nanoparticles. The crystalline size was analyzed using X-ray diffraction. The particle size has been calculated using scherrer equation. The optical study helps to determine the band gap value. The chemical composition of the formed MnO_2 nanoparticle has been concluded from FTIR study. The size and shape of the synthesized MnO_2 nanoparticle have been defined with the help of XRD and HRTEM study. Thermal stability of synthesized MnO_2 nanoparticle has been analyzed with the help of TG study. Electrical conductivity of MnO_2 have is in the order of $2.35 \times 10^{-7} Scm^{-1}$as calculated from AC impedance spectroscopy.

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