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RESEARCH ARTICLE

SYNTHESIS AND STRUCTURAL INVESTIGATION OF MN_3O_4 NANOPARTICLES BY MICROWAVE - ASSISTED SOLUTION METHOD

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ABSTRACT

Trimanganese tetraoxide (Mn_3O_4) nanoparticles have been synthesized via simple Microwave Assisted solution method. The structural investigation was carried out using powder X -ray diffraction. It showed that the Mn_3O_4 nanoparticles present in tetragonal hausmannite structure and their grain sizes were estimated from Particle size analyser, XRD and High Resolution Transmission Electron Microscopy images. The size of the Mn_3O_4 nanoparticles is around 20 - 24 nm. The Mn_3O_4 nanoparticles were characterized by X-ray diffraction, Particle size analyzer, HRTEM, FTIR and SEM studies.

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INTRODUCTION

Nanomaterials feature high surface energy and reactivity resulting from their high specific surfaces and exhibit special electric, magnetic, absorptive, and catalytic properties [1–6]. Manganese oxides have different forms such as MnO2, Mn2O3, Mn3O4, and MnO due to its different oxidation states. Among the above mentioned structures, Mn3O4 is one of the stable mixed oxides state ($Mn^{2+}(Mn^{3+})2O4$) and having spinel structure. Trimanganese tetra oxide are particularly interesting in view of its widespread use in many applications, such as batteries, high-density magnetic storage media, electro-chromic materials and catalysts [7–10] and also used as an effective catalyst for the decomposition of waste gas and Mn3O4 act as a suitable material to control the air pollution [11]. The properties of semiconductor nanostructured materials depend not only on their chemical composition but also on their shape and size. Mn_3O_4 was often synthesized by the high-temperature calcination of either higher manganeseoxides (MnO_2, Mn_5O_8, and Mn_2O_3), or MnII and MnIII oxysalts, hydroxides, or hydroxyoxides [12]. In the last decade, various different shape and size Mn3O4 nanocrystals have been synthesized by various techniques, for instance, single-crystal Mn3O4 nanorods were obtained by a simple chemical method [13]; nanoparticles were prepared by oxidation precipitation method [14,15], vapor phase growth [16] and thermal decomposition [17,18]; hierarchical structure with radiated spherulitic nanorods was prepared via a simple solution-based coordinated route, or under mild and organic free template [19,20]; porous hexagonal plates were prepared by a hydrothermal method [21]; thin films were prepared by chemical bath deposition [22]; nano fibers were prepared by sol–gel process [23]; three dimensional nanostructures were synthesized by soft chemistry templating process [24]. However, the exploration of low-temperature routes for the synthesis of Mn3O4 has, therefore, been worth attempting. Recently, nanocrystals like rods were obtained by one-step room-temperature synthesis [25] or by hydrothermal and solvothermal process [26,27], g- Mn3O4 nanorods were also gained by one-step low-temperature alcohol–water thermal route [28], the uniform and ligand capped nanocrystals with hausmannite structure could be prepared from MnO by controlled chemical oxidation [29,30]. More and more research has been focused on the synthesis of Mn_3O_4 nanoparticles in recent years and some synthesis methods have been developed. Among the various synthesis methods, microwave assisted solution method possess the added advantage of faster reaction time than the conventional solvothermal method. Here, the

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Mn3O4 nanoparticles were prepared at a less reaction time compared to the reaction time of other methods. However, in this study, the Mn3O4 nanoparticles were prepared using microwave assisted Solution method. The characteristics such as crystallinity, presence of functional groups, thermogravity, and morphology were analyzed using various techniques.

Experimental

MATERIALS

All the chemicals were used as analytical grade without any further purification. Manganese chloride tetrahydrate [MnCl2.4H2O] (AR grade LOBA), Ethylene glycol [EG] (AR grade LOBA) and sodium hydroxide [NaOH] (AR grade MERCK) were used to prepare the nanoparticls of this work. Water used in this investigation was de-ionized water.

Synthesis of Mn_3O_4 nano particles

Trimanganese tetraoxide (Mn_3O_4) nanoparticles was synthesized as follows: the precursors like Manganese chloride tetrahydrate [MnCl2.4H2O] and Sodium hydroxide (NaOH) were taken in 1:4 molar ratio and dissolved completely in de-ionized water separately. Then the dissolved MnCl2.4H2O was added with EG. Further the NaOH solution was added drop wise into the above mixture under vigorous stirring until the color of the solution was changed into brown color. Then the prepared mixture solution was kept in the microwave oven (900 W, 2450 MHz, Onida, India) at a temperature of 50^{o}C for about 30 minutes. Finally, the as prepared sample was centrifuged several times in double distilled water, ethanol and dried at 150 ˚C for 24 hours results in the formation of Mn_3O_4 nanoparticles.

Instrumentation

Powder X-ray diffraction pattern of the nanoparticles was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu K_α radiations with λ= 1.54056 Å at 35 kV, 10 mA). The sample was scanned over the required range for 2Θ values (10 – 80^o). The particle size analysis for the sample was carried out using the particle size analyzer (Zetasizer Ver. 6.20 , Serial Number : MAL1049897). The size and shape of nano particles was obtained by high resolution transmission electron microscopy (HRTEM) and HRTEM measurements were carried out on a JOEL JEM 2000. The FTIR spectrum of the sample was recorded using a Shimadzu 8400S spectrometer by the KBr pellet technique in the range 400-4500 cm^{-1}. The morphologies of the as-prepared samples were investigated through Scanning Electron Microscopic (SEM) images. The SEM images were taken for the nano powdered samples using Model Hitachi SEM S 2400 device.

RESULTS AND DISCUSSIOSN

Structural characterization

X-ray diffraction(XRD) studies

The powder XRD pattern for the as-prepared pure Mn_3O_4 nanoparticles is presented in the figure 1. It is observed that the XRD reflection peaks for pure Mn_3O_4 sample are in a perfect match with the diffraction pattern of Mn3O4 published in the (JCPDS File No. 24-0734). All the reflections of powder XRD patterns of this work were indexed using the TREOR and INDEXING software packages. The diffraction peaks of the as prepared Mn3O4 samples at 2θ = 17.98,28.88, 32.33, 36.1, 38.01, 44.46, 50.71, 58.39, 59.86, and 64.73° corresponds to the Miller indices or lattice planes of (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) respectively. Therefore, it can be indexed to the tetragonal hausmannite structure (space group *I*41/ amd) of Mn3O4. The powder XRD pattern of Mn_3O_4 nano particles shows broad peaks, which confirmed the formation of small-sized nanoparticles. The particle size of nano particles was determined using the Scherrer's relation d= $(0.9\lambda)/(\beta\cos\theta)$ where β is the full width at half maximum in radians, λ is the wavelength of X-rays used and θ is the Bragg's angle. For the various reflection peaks of the XRD pattern, the particle size was estimated and the average size of nano particles of the sample was found to be around 20 nm. The less intensity of diffracted peaks reveals that the low crystallinity of the as prepared samples. The lattice constants, lattice density, and cell volume of the samples are calculated and are tabulated in Table 1. The obtained lattice constant values are *a*=*b*= 5.769 Å, *c*= 9.46 Å. These values are in good agreement with the reported values [31-33]. The particle size analysis for the sample was carried out using the particle size analyzer (Zetasizer Ver. 6.20 Serial Number : MAL1049897). The particle size distribution is presented in the Fig. 2 and it is observed that the size of maximum number of particles is 24.36 nm. It is in good agreement with the particle size observable on the XRD spectrum.

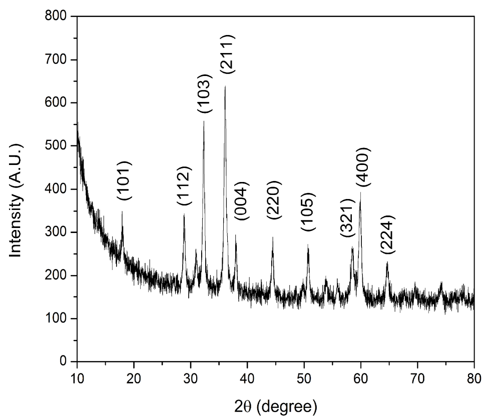

Fig 1 XRD Pattern of as prepared Mn_3O_4 Nanoparticle

Table 1 Structural parameters of Mn_3O_4 samples.

Lattice Constant Calculated (A°)	Lattice Constant Standard (A°)	Grain size in nm	Cell Volume Calculated (A°)	Cell Volume Standard (A°)	Lattice density (g/cm^3)
a=b= 5.7699 c= 9.466714	a=b= 5.763 c= 9.456	24	315.159	314.05	4.822

High ResolutionTransmission Electron Microscopic (HRTEM) studies of Mn_3O_4 nanoparticles

The information such as particle size, size distribution, shape, degree of agglomeration etc of Mn_3O_4 nano particles are obtained from High Resolution Transmission Electron Microscopy (HRTEM).

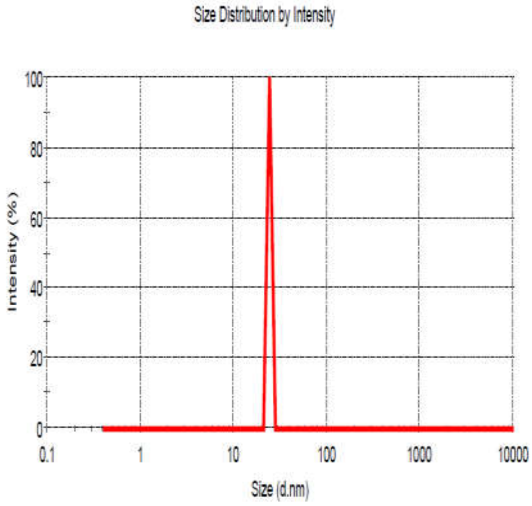

Fig 2 Particle size analyzer spectrum of Mn_3O_4 nanoparticles

The HRTEM overview images were presented in Figs. 3(a), 3(b) and 3(c). From the images it is concluded that the nano particles are of uniform in size and shape. It is observed that the shapes of most of the particles are nearly spherical and slightly elongated. To obtain a particle size distribution from transmission electron micrographs we manually measured the particle sizes for 50 particles to ensure a reliable representation of the actual size distribution. The crystallite size is about 20-40 nm as estimated from the HRTEM micrographs. The experimental and calculated XRD patterns provide a volume-weighed average grain size of 24 nm, which is in good agreement with the particle size observable on the HRTEM image.

The selected area electron diffraction (SAED) pattern of Mn_3O_4 nano particle is shown in the Fig. 3(d), The high crystallinity of the powder leads to its corresponding well-pronounced Debye-Scherrer diffraction rings in the SAED pattern that can be assigned to the reflections (101), (112), (103), (211), (004), (220), (105), and (400) of tetragonal hausmannite structure of Mn3O4. There are no additional rings in the SAED pattern stemming from any crystalline impurities. To get further insight into the atomic order of the Mn_3O_4 nanoparticles, high-resolution images were recorded

Fourier Transform Infra Red (FT-IR) Analysis

The presence of functional groups in Mn_3O_4 samples are identified through FTIR analysis. Figure. 4, shows the FT-IR spectra of Mn_3O_4 samples. The samples show a broad band around 3401 cm^{-1} indicating the presence of –OH group in the as prepared samples. The small bands are observed at approximately 1628 cm^{-1} and 1382 cm^{-1} corresponds to the adsorption of molecules from moisture and bending vibration of O-H joined with metal (Mn) atoms. The two significant peaks observed at approximately 613, 504 and 410 cm^{-1} that reveals the coupling between the Mn-O stretching modes of tetrahedral and octahedral sites respectively. That is, the vibration band around 613 cm-1 corresponds to the characteristics of Mn-O stretching mode in tetrahedral sites, similarly the vibration band observed around 504 and 410 cm^{-1} is associated with distortion vibration of Mn-O in an octahedral site [31,34-36].

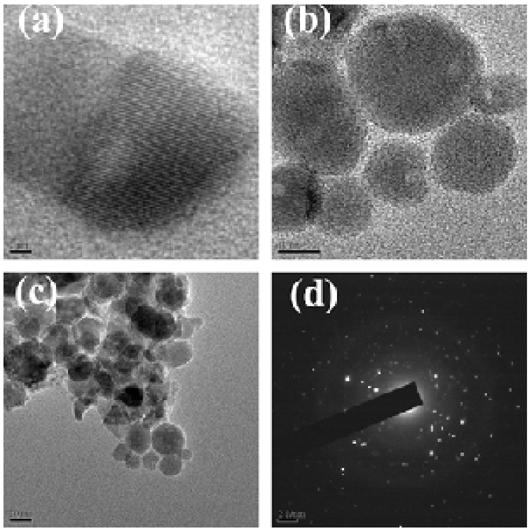

Fig 3 (a,b,c) HRTEM images of the Mn_3O_4 nanoparticles and (d) SAED pattern for one agglomerated of Mn_3O_4 nanoparticles.

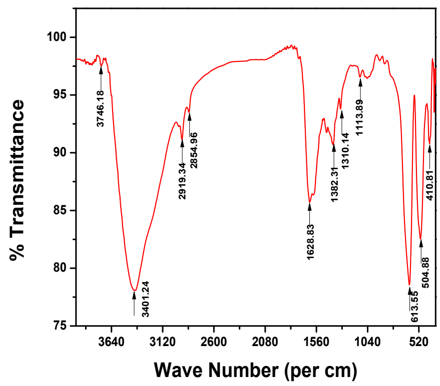

Fig 4 FTIR spectra of the Mn_3O_4 nanoparticles

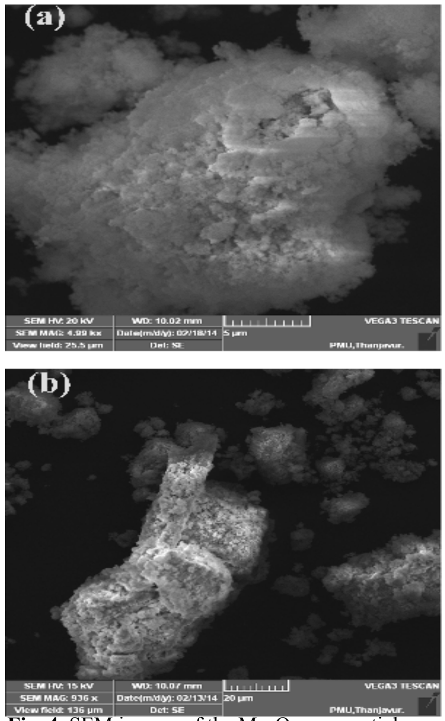

Fig 4 SEM images of the Mn_3O_4 nanoparticles

Scanning Electron Microscopic (SEM) studies of Mn_3O_4 nanoparticles

The figure.4 show the SEM images of Mn3O4 at different magnification. It can be seen that the particles are well defined in the size ranging in nanometer level. However, some particle agglomeration is also observed. This aggregation of nano particles is due to the effect of microwave heating because it forms the hot surface on primarily formed nano particles. It Indicates that Mn_3O_4 nano particles exhibits a sheet-like morphology and consists of numerous flower- like aggregates with multi-leaves, where each flower is made up of many thin nanoparticles assembled to form the observed architecture [37,38]. Such flower-like morphology is similar to the one described by Pan *et al*. [39], which deemed that the nanosheets were spokewise, projected from a common central zone. The results obtained in this work were found to be in agreement with the work obtained by other researchers.

CONCLUSION

In summary, Mn_3O_4 nano particles were prepared by microwave assisted solution method. X – ray structural analyses confirmed that Mn_3O_4 nano particles crystallize in the tetragonal hausmannite structure. From XRD and TEM results, Mn_3O_4 nanoparticles exhibit crystallite size between 20 -24 nm. It is confirmed by Particle size analyser and TEM studies. The functional groups of the sample have been identified from FTIR studies. The morphology of the sample has been examined by SEM.

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