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Fabrication of Hetarolite-ZNMN$_2$O$_4$ by Solvothermal Method and its Nanostructural Characterization

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Abstract

Hetarolite-$ZnMn_2O_4$ nanoparticles were synthesized by hydrothermal/solvothermal method using Mn $(CH_3COO)_2{\cdot}4H_2O$ and $Zn(CH_3COO)_2.2H_2O$ as precursors and Oleic acid as surfactant at synthesis temperature of 180ºC for 48hr. The synthesized product was characterized by X-ray Powder Diffraction (PXRD), Field Emission Scanning Electron Microscopy (FE-SEM), and Energy Dispersive X-ray analysis (EDAX), High Resolution Transmission Electron Microscopy (HR-TEM), Selected Area Electron Diffraction (SAED), UV-vis-NIR absorption and Fourier Transform Infrared Spectroscopy (FTIR). The XRD analysis reveals that $ZnMn_2O_4$ nanoparticles exhibit tetragonal structure. The functional group of$ZnMn_2O_4$is confirmed from FTIR spectral study. The optical property of the sample is discussed from the Uv-vis-NIR absorption spectrum. The chemical composition is confirmed by EDX analysis. The effect of the surfactant, the preparation technique on the crystallite size and distribution is discussed by analyzing the Selected Area Electron Diffraction (SAED) patterns of the synthesized nanoparticles.

Keywords: Solvothermal, Surfactant, Nanoparticles, Tetragonal.

Introduction

Today, nanotechnology (NT) is operating in various fields of science via its operation for materials and devices prepared using different techniques at nanometer scale. Nanoparticles are a part of nanomaterials that are defined as single particles of 1–100 nm in diameter[1].Nanometer-sized materials have recently attracted a considerable amount of attention due to their unique electrical, physical, chemical, and magnetic properties[2].These materials behave very differently from bulk materials.Hetarolite-$ZnMn_2O_4$ is one of the most attractive compounds of the AB_2O_4 series because of its low oxidation potential and low material cost[3]. Various nanostructures of Hetarolite- $ZnMn_2O_4$ with different morphologies such as, nanorods/nanowires, mesoporous/hollow spheres, nanofibers and other structures have been synthesized by different routes, such as sol-gel process, thermal decomposition, co-precipitation, microwave synthesis, and hydrothermal process etc[4-5].**Pei Fan Tehv** reports on $ZnMn_2O_4$ powders (nanofibers, nanorods, nanowebs) synthesized via facile electrospining technique by a simple variation of sintering profile which has potential application as anodes in lithium ion battery[6].**L.Xiao et al** reported the electrochemical properties of flower –like $ZnMn_2O_4$ super structure, which can also be used for lithium-ion-batteries storage application[7].**Zhang et al** prepared one –dimensional $ZnMn_2O_4$nanorods viahydrothermal method using metal acetate as precusor at 140ºC for 12h[8].The formation of $ZnMn_2O_4$ hollow microspheres by $ZnMn_2O_4$nanosized building blocks, demonstrated by **L.Zhou et al** ensures better structural stability & cyclability as an anodic material for lithium –ion-batteries[9]. **Bessekhonad and Trari** prepared spinel $ZnMn_2O_4$ powder by solid state reaction under high temperature [11]. **L.Zhao et al** synthesized cubic $ZnMn_2O_4$nanoparticles using hydrothermal method at 180ºC for 24h[10].**Fan et al** successfully synthesized 1D single–crystalline spinel MFe_2O_4nanotubes/nanorings by thermal transformation process where $ZnMn_2O_4$nanorods were successfully prepared using the α–MnO_2 nanorods as templates[12]. **Asbrink et alv** synthesized $ZnMn_2O_4$ with a normal spinel structure having a tetragonal distortion (c/a=1.14) of the face centered pseudo cubic cell with cell parameters of a=8.087 and c=9.245Å.

In this work, we report the solvothermal synthesis technique of preparing Hetarolite - $ZnMn_2O_4$nanoparticles using ethanol as solvent and metal acetates as solute. Oleic acid (OA) is a commonly used surfactant to stabilize the metal oxide nanoparticles with strong chemical bond between the carboxylic acid and the amorphous Zinc manganese oxide nanoparticles. For this material Hetarolite-

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$ZnMn_2O_4$, we report the role of oleic acid as the surfactant in the synthesis which controls the particle size as well prevents the nanoparticles from aggregation.

Experimental

Materials:

Manganese acetate Mn $(CH_3COO)_2$.$4H_2O$, Zinc acetate Zn $(CH_3COO)_2.2H_2O$, Oleic acid and absolute ethanol from Merck Company are of analytical grade and were used without further purification. Only Deionized water was used for the preparation.

Sample preparation:

The synthesis of Hetarolite- $ZnMn_2O_4$nanoparticles was carried out via a solvothermal treatment method. In a typical procedure, 3mmol of Mn $(CH_3COO)_2.4H_2O$ and1.5mmol of Zn $(CH_3COO)_2.2H_2O$ were dissolved in 80 ml of absolute ethanol. After stirring for 30min, 0.2g of oleic acid was added, to form a homogeneous solution. The obtained solution was then transferred into a 150 ml Teflon- lined stainless steel autoclave sealed and maintained at 180ºC for 48 h. The autoclave was then cooled to room temperature naturally, and the resulting brown precipitated powder was separated by centrifugation, washed with anhydrous ethanol several times, dried in a vacuum at 80ºC for 24 h.

Sample characterization:

The structures of the final products were characterized by powder X-ray diffraction. The Powder X-ray Diffraction pattern was recorded on RICH SEIFERT X-ray powder diffractometer with a monochromatic nickel filtered CuKα (λ=1.5406Å) radiation. The morphology and size of the resultant products were characterized by JEOLJSM6310. Field-Emission Scanning Electron Microscope (FE-SEM) that operated at 15 kV. Energy Dispersive X-ray spectrum (EDX) revealed the chemical composition of the sample. The High-Resolution Transmission Electron Microscope (HRTEM) images and Selective Area Electron Diffraction (SAED) patterns obtained using JEOL JEM-2100 microscope which operated at 200kV gives detailed information about the crystal planes, size and distribution of the nanoparticles. In the preparation of samples for TEM observation, the materials were first dispersed in ethanol using an ultrasonic bath for 10 min and then dropped onto a copper grid, which was dried in air at room temperature and kept in vacuum before TEM observation. The Fourier Transforms Infrared (FTIR) spectra were recorded at 20ºC using 'Perkin Elmer' model. The specimens were pressed into small disks using a spectroscopically pure KBr matrix. A Ultra-violet visible (UV-vis) Lambda 35 spectrophotometer in arrange of 200 to 1100nm was used to study the optical absorption. The optical band gap was determined by analyzing the data obtained.

Result and discussion

XRD analysis:

The crystalline structure and phase purity of the obtained product determined by XRD are as shown in fig.1. All the diffraction peaks can be exclusively indexed to that of a pure tetragonal phase of $ZnMn_2O_4$ with a lattice constant of a=b=5.762 Å, c=9.470Å and space group of $I4_1/amd$, which is in good agreement with the JCPDS data (JCPDS.No:24-1133) reported in literature. The average crystallite size was estimated using Scherrer formula,

$$D = \frac{K\lambda}{\beta COS\theta}$$

Where D is the crystallite size, K is the shape factor, λ the X-ray wave length, θ the Bragg's angle in radians, and β the full width at half maximum in radians. The crystallite size thus obtained from the preferentially oriented peak of (211) plane was found to be 24nm.

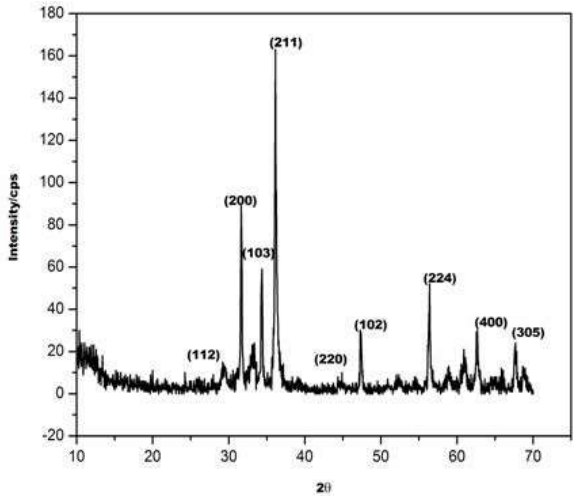

Fig.1, XRD pattern of $ZnMn_2O_4$

FTIR analysis:

FTIR analysis which was recorded in the range of 400-4000$cm^{-1}$are shown in fig.2. In the region from 700 to 500cm^{-1}, two absorption peaks were observed at 667.9 and 556.9cm^{-1}, which are associated to M-O (M=Zn,Mn) and M-O-M stretching mode of tetrahedral and octahedral respectively .The weak band at 1114.2 cm^{-1}, which can be attributed to Mn-O-H vibration of ethanol molecules on the surface of the Hetarolite ($ZnMn_2O_4$) particles. More over the band between3800cm^{-1} and 2200cm^{-1} is due to the O-H stretch of the carboxylic acid group of oleic acid. The Weak shoulder at 1616cm^{-1}can be assigned to the C=C stretching mode for oleic acid. A strong

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adsorption at 1330.2 and 1407.25cm^{-1} arises from C-O single bond stretching. These results revealed that Oleic acid were chemisorbed on to the Hetarolite -$ZnMn_2O_4$nanoparticles as a carboxylate.

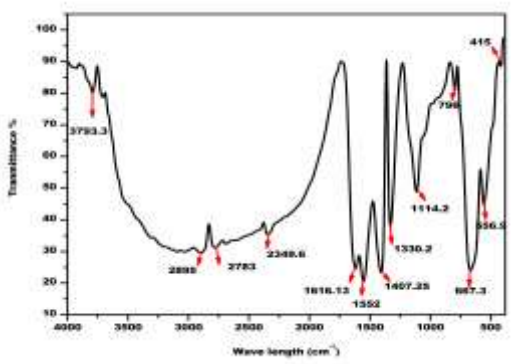

Fig.2, FTIR spectrum of $ZnMn_2O_4$

FESEM analysis:

The morphology and nanostructural details of the as prepared the Hetarolite -ZnMn2O4nanoparticles were investigated by FESEM. Fig3(a), shows a low magnification FESEM image of the as-obtained product. It may clearly be found that the as-obtained product possesses nanowire like structure. Further,high magnification FESEM imagesreveal the transformation of wire like strucutre into almost numeroulyassembled spherical shaped nanoparticle with size of about 18nm as shown in fig3(b).

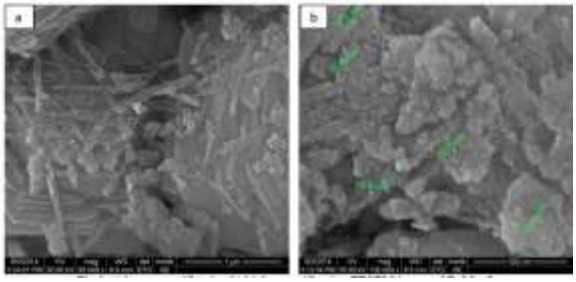

Fig.3, a) low –magnification b) high-magnification FESEM image of $ZnMn_2O_4$

On Keeping the same reaction conditions the amount of oleic acid is changed to investigate the effect of oleic acid on the morphology of the obtained materials ,and the experimental results are shown in figs.4a,b,c. For 0.2 g of oleic acid(fig.4a) used in the hydrothermal synthesis, the particleshave nanowire like structure. On increasing the amount of oleic acid to about 0.3g(fig.4b), the morphology of the particles obtained is irregular spherical shape.Onfurther increase of oleic acid to 0.4g(fig.4c),the particle size becomes large and some of the microspheres crack.

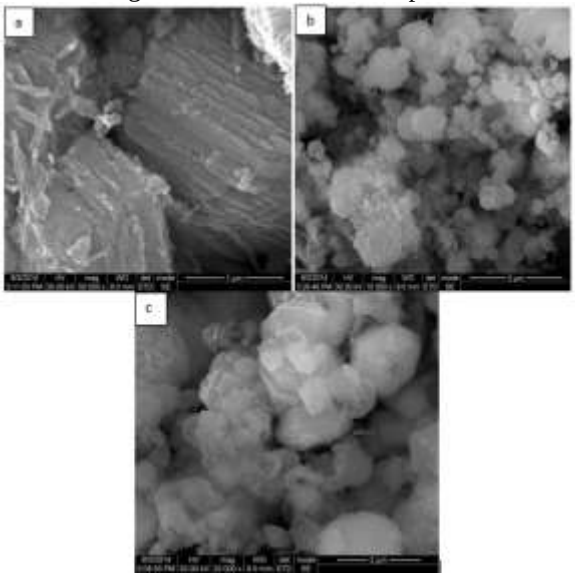

Fig.4, FE-SEM image of$ZnMn_2O_4$ with different amount of oleic acid a) 0.2mmol, b) 0.3mmol.c)0.4mmol.

EDX:

The composition of obtained nanoparticles was then analyzed by Energy-dispersive X-ray (EDX) spectroscopy as shown in fig5(a).It was found that the product was composed of the following elements Mn, Zn and O. No other peak related with any impurity has been found in the EDX, which demonstrates that, the Hetarolite -ZnMn2O4 are composed only with Mn, Zn and O.

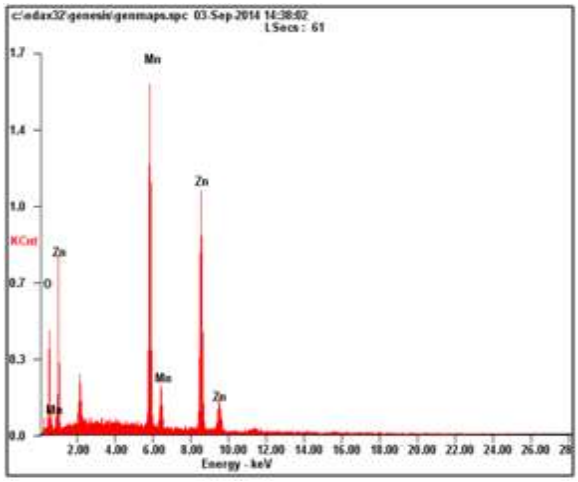

Fig.5, EDX spectrum of $ZnMn_2O_4$ Nanoparticles

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TEM analysis:

Further the morphological characterization was alsocarried out by the high resolution transmission electron microscopy (HR-TEM) and equipped withthe selected area electron diffraction (SAED) pattern.Figure 6 shows the low and high magnification HR-TEM image of ZnMn2O4 naorod like particles grown at 180ºC. The HR- TEM imageis clearly consistent with the FESEM observations,indicating the polycrystalline nature of the ZnMn2O4 nanoparticles.The inter planer spacing'd' (distance of two successive lines), measured from the fringe pattern are0.2488 and 0.270nm corresponds to the (211) and (103) plane which is also observed in XRD study, shown in fig1. Fig. 7 shows the selected area electron diffraction pattern (SAED) originated from the spinel ZnMn2O4 and the planes calculated from the diffraction rings are same with the planes obtained from our XRD study. Therefore ,it could be concluded that the solvothermal synthetic method is able to prepare well –crystallized ZnMn2O4nanoparticle at a temperature as low as 180ºC.

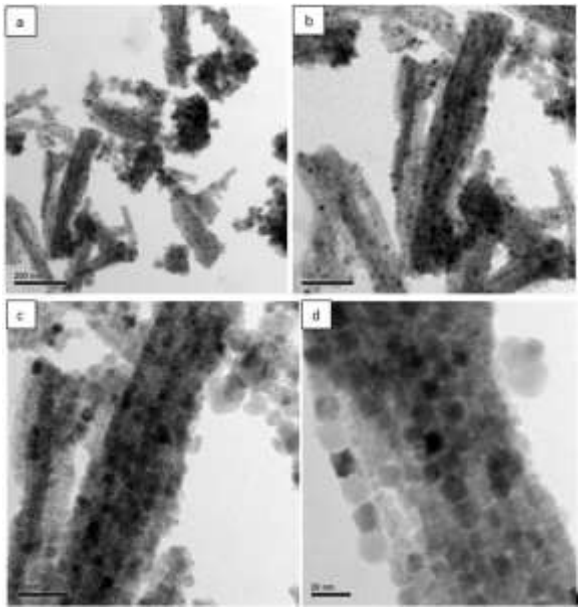

Fig.6, Low and high magnification HR-TEM image of $ZnMn_2O_4$ Nanoparticles.

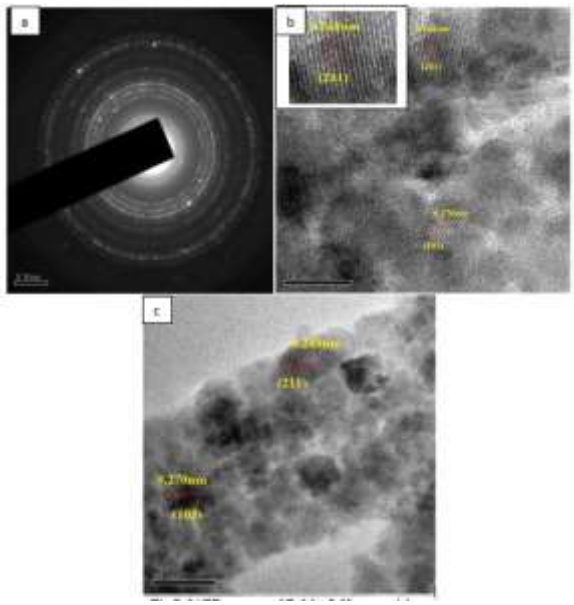

Fig.7, SAED pattern of ZnMn2O4Nanoparticles.

UV-VISIBLE SPECTROSCOPY:

UV-Visible absorption, and band gap spectra for Hetarolite -ZnMn2O4nanoparticles are shown in Figure .8. The spectrum shows the band edge- absorption peak which is found to be at 233nm. In UV-Vis, high energy electromagnetic radiation in the wavelength range of 100-700nm is utilized to promote electrons to higher energy orbital's. From the UV spectra, it is clear that he absorbance decreases with increase in wavelength. This decrease in the absorption indicates the presence of optical band gap in the material. The relation between absorption coefficients (α) and the incident photon energy (hυ) is given by the equation,

$\alpha h\upsilon = A\,(h\upsilon - E_g)^n$

Where A is a constant .E_g is the band gap of the material and the exponent 'n 'depends on the type of transition n=1/2,2,3/2&3 corresponding to allowed direct, allowed indirect ,forbidden direct, forbidden indirect respectively. Taking n=1/2, the direct energy band gap is calculated from the $(\alpha h\upsilon)^{1/n}$ Vs hυ plots(fig). The estimated band gaps of the sample is found to be 1.54eV

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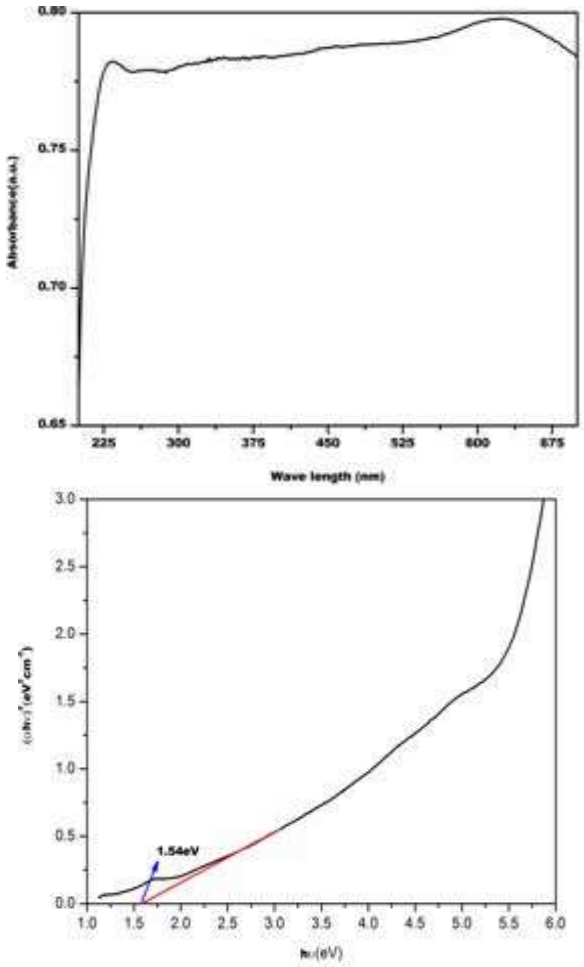

Fig.8, UV-Vis spectrum and $(\alpha h\upsilon)^2$vs hυ graph

Conclusion

This study demonstrates the fact that manganese acetate and zinc acetate are a proper precursor for the formation of Hetarolite -$ZnMn_2O_4$ nanoparticles. The XRD pattern confirms that the Hetarolite -$ZnMn_2O_4$is formed in the tetragonal spinel structure. FTIR spectrum reveals that the sample prepared has the finger print of Hetarolite -$ZnMn_2O_4$nanoparticles. The major stretching and bending vibrational frequencies have been identified. Hetarolite -$ZnMn_2O_4$ nanoparticles were prepared by Solvothermal method using different amount of surfactant. Oleic acid was used as a surfactant in the formation of Hetarolite -$ZnMn_2O_4$. FESEM images confirm the formation of nano-fiber like rod structures. TEM studies confirm
the growth of Hetarolite -$ZnMn_2O_4$ nanoparticles is polycrystalline nature.

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