International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.5, pp 2138-2143, 2014-2015

ICONN 2015 [4th - 6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Synthesis and characterization of nickel oxide, manganese oxide nanoparticles and NiO/MnO nanocomposite: hydrothermal approach

Swetha .J. V and Geetha. A*

Department of Physics and Nanotechnology, SRM University, Kattankulathur, Chennai 603203, India

Abstract: Manganese oxide, nickel oxide nano particles and nickel-manganease oxide nano composites were synthesized by hydrothermal method using potassium permanganate and nickel chloride hexa hydrate as a starting materials. The synthesized nano particles and nano composites were characterized by means of X-ray diffraction, scanning electron microscopic, energy dispersive X-ray and UV-Vis spectroscopic studies and X-ray florescence spectroscopic studies. The crystallite size of the synthesized nanoparticles and nano composites were obtained from X-ray diffraction study using Debye-Scherer formula and it was found to be 12nm for MnO, 14nm for NiO and 5.5nm for NiO/MnO nanocomposite. The surface morphology of nickel/manganese oxide nanocomposites was analyzed by scanning electron microscopic study and it was analyzed as rod like structure. The optical properties were analyzed using UV-studies.

Keywords: nano composites, manganese oxide, nickel oxide, hydrothermal method.

Introduction

In the recent years, the various size and shape of different nanomaterials has been realized through a wet-chemical synthesis because of its wide range of application. Owing to this reason researchers showing an increasing interest to fabricate nanostructured materials[1]. In this present work we prepared nano particles and nanocomposites using wet-chemical synthesis[2]. Its applications are extended by changing its physical and chemical properties under nanoscale due to large range of surface to volume ratio[3]. The chosen metal oxide nanoparticles like manganese oxide and nickel oxide is an important transition metal oxides of p-type semiconducting materials with a band gap of 3.3 eV and 3.8 eV[4,5]. These metal oxide nanoparticles and metal oxide nano composites were used as a gas sensors, electro chromic films and fuel cells etc. Generally nanocrystalline metal oxides and metal oxide nanocomposites have been prepared by wet-chemical techniques such as sol-gel, solvothermal and co-precipitation methods etc[6,7]. Here we prepared NiO, MnO nanoarticles and NiO/MnO nano composites by using hydrothermal method[6].

Experimental

Preparation of MnO, NiO nanoparticles:

All Chemicals purchased from E-Merck with 99.9% of purity which is used as received without further purification. The nano materials were synthesized by hydrothermal method. The manganese oxide nanoparticles was synthesized by taking 0.1 M of $KMnO_4$, 0.05M of CTAB and 0.05M of urea and it was dissolved in D.I water. The solution was stirred with half an hour at room temperature and it was transferred to a Teflon lined stainless steel auto clave with 100 ml capacity and it is placed in an electric oven for 12h at 150^0c. The product was centrifuged and again placed in an electric oven dried for 12h at100^0c .The obtain product was MnO nanoparticles. The same procedure was adopted for the preparation of NiO instead of $KMnO_4$ we used $NiCl_2.6H_2O$ as a precursor material[8].

Preparation of NiO/MnO nanocomposites:

NiO/MnO [(0.1/0.1)M] nanocomposites were prepared by using hydrothermal method. $KMnO_4$, CTAB, $NiCl_2.6H_2O$ and urea was used as starting materials. 0.1M of $KMnO_4$, 0.1M of $NiCl_2.6H_2O$, 0.05M of CTAB and 0.05 M of urea were dissolve in 50 ml of D.I water. The solution was stirred with half an hour at room temperature and it was transferred to a Teflon lined stainless steel auto clave with 100 ml capacity and it is placed in an electric oven for 12h at 150^0c. The product was centrifuged and again placed in an electric oven dried for 12h at100^0c. The obtained product was named as NiO/MnO nano composite[8]. The colour of MnO is blue color and NiO is a green color when NiO is added with MnO the color of NiO/MnO nano powders changes to black color. The prepared NiO/MnO nano composite was characterized for their structural, optical and surface morphological properties. X-ray diffraction pattern (XRD) were recorded using X-ray diffractometer (X' Pert PAN Analytical) with CuKα radiation (λ=1.5405Å). Morphological studies were carried out using scanning electron microscope (FEI Quanta 200 FEG). XRF analysis was carried out using X-ray Flurorecence spectroscopy (Philips X'Pert PAN Analytical). Optical properties were studied using UV-Vis Spectrophotometer (Shimadzu 2450).

Results and Discussion

Structural Analysis Studies for MnO and NiO nanoparticles and NiO/MnO nanocomposites:

Pure Mno nanoparticles:

Fig.1 shows the XRD pattern of the pure Mno nano particles prepared using hydrothermal method. The XRD peaks were indexed as (111), (201) and (080) planes by comparing with the JCPDS file (card No: 04-0326) which clearly indicates MnO nano particles are of orthorhombic system. From the XRD peak, the MnO average crystallite size of particles was calculated from Debye Scherer formula-

$D= 0.9\lambda/ (\beta\cos\theta)$

Where λ is the wavelength of X-rays used (1.5405Å), β is the Full Width Half Maximum (FWHM) in radian and θ is the angle of diffraction. The calculated average crystallite size from the XRD peaks for pure Mno nanoparticles was found to be 14nm[9].

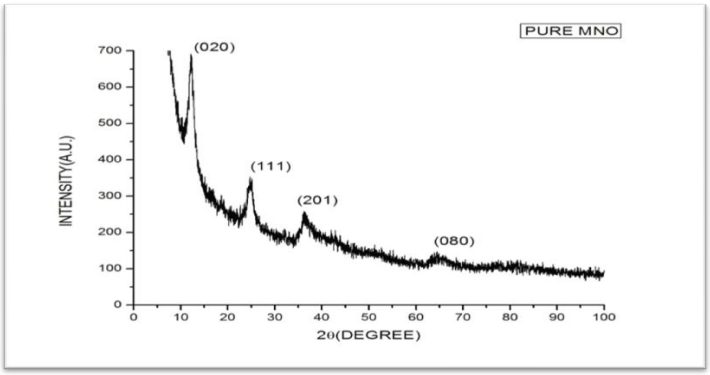

Fig.1 XRD pattern of Pure MnO nanoparticles

Pure NiO nano particles:

Fig.2 shows the XRD pattern of the NiO nanoparticles prepared using hydrothermal method. The XRD peaks were indexed as (111), (200), (220) and (311) planes[10] by comparing with the

JCPDS file (card No:47-1049) which clearly indicates NiO nanoparticles of cubic structure. From the XRD peak, the NiO average crystallite size of particles was also calculated from the above Debye Scherer formula and it was found to be 12nm[10].

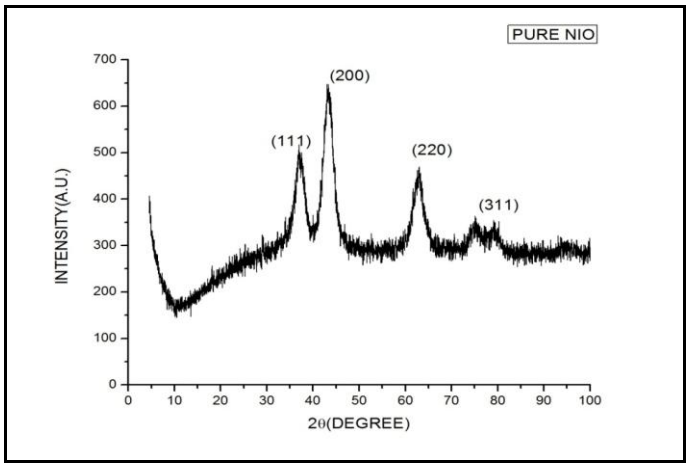

Fig.2 XRD pattern of NiO nanoparticles

NiO/ MnO nanocomposites:

Fig.3 shows the XRD pattern of NiO/MnO nanocomposites synthesized by hydrothermal Method. The XRD peaks (111), (201) and (080) were confirming the formation of NiO/MnO nanocomposite[11]. The stronger peaks are coinciding with the JCPDS file (No: 04-0326) which shows the crystal structure of MnO belonging to orthorhombic system and the week peaks like (220) and (400) matching with the JCPDS file (No: 47-1049) shows the crystal structure of NiO belonging to the cubic system. The XRD analysis reveals that the prepared nanocomposite has composed of cubic NiO and orthorhombic MnO. From the XRD pattern, the average crystallite size of NiO/MnO nanocomposites was calculated from Debye Scherer Formula and its value was calculated as 5.5 nm.

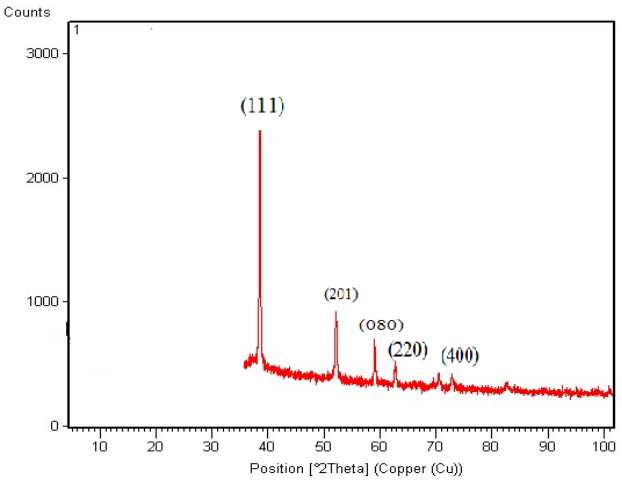

Fig.3 XRD pattern of NiO/MnO nanocomposites

Morphology Analysis Of NiO/MnO Nanocomposites:

The size and morphology for the NiO/MnO nano composites was characterized using SEM studies. Fig 4(a),4(b) and 4(c) shows the SEM images morphology of NiO/MnO nano composites with diffent magnifications.The SEM images clearly indicates that nano rod shape of NiO/MnO particles are formed and they are agglomerated to form large size structures.For conformation of Mn^{2+} and Ni^{2+} ions present in the

sample .we carried out the EDAX study of the prepared NiO/MnO nano composite[12]. The fig. (5a) shows the EDAX specturm of NiO/MnO nano composites. The EDAX spectrum shows the peaks corresponding to Mn^{2+}, Ni^{2+}, and O^{2+} . The EDAX measurements of the nanocomposite show that contains atomic percentage of nickel (50.97 %), manganease (16.1 %) and oxygen (33.2 %), which is roughly similar to the calculated values. For further confirmation of the elemental composition of the prepared nanocomposite, XRF analysis was carried out . The XRF spectrum (Fig. 5b) shows energy peaks corresponding to Manganese, Nickel and Oxygen. The XRF and EDAX analyses confirms that the prepared nanocomposite have elemental composition of Mn^{2+}, Ni^{2+} and O^{2+}.

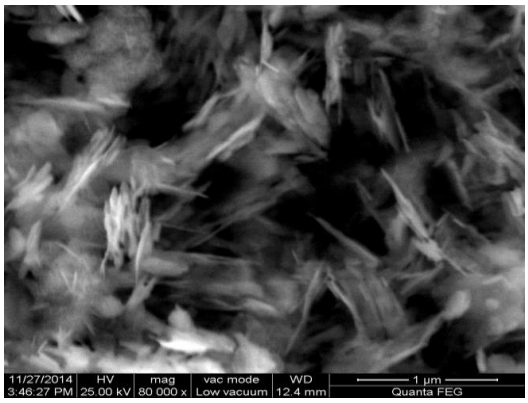

Fig.4(a) SEM image of NiO/MnO nanocomposite with 1micrometer

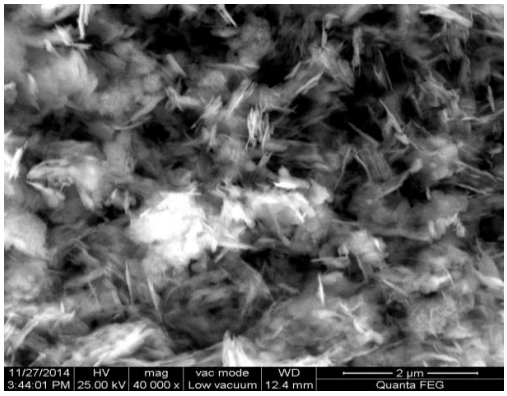

Fig (4b) SEM image of NiO/MnO nanocomposite with 2 micrometer

/

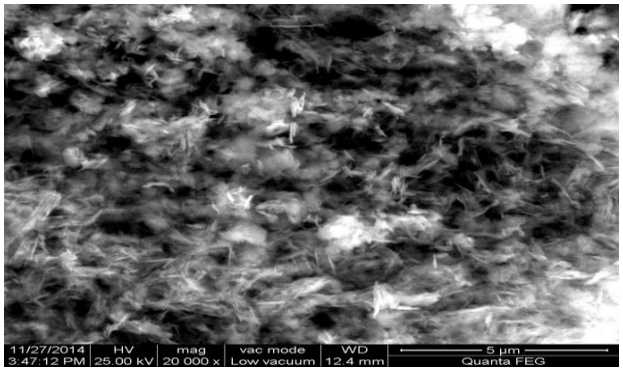

Fig.4(c) SEM image of NiO/MnO nanocomposite with 5 micrometer

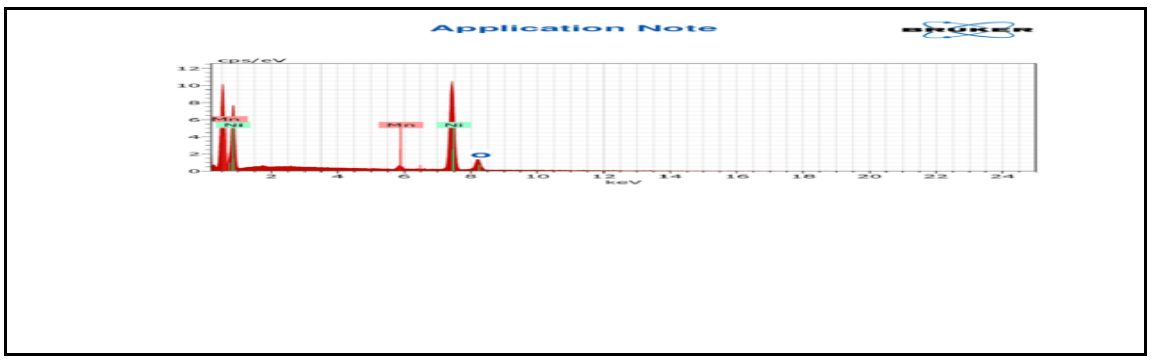

Fig .5a- EDAX Spectrum for NiO/MnO nanocomposites.

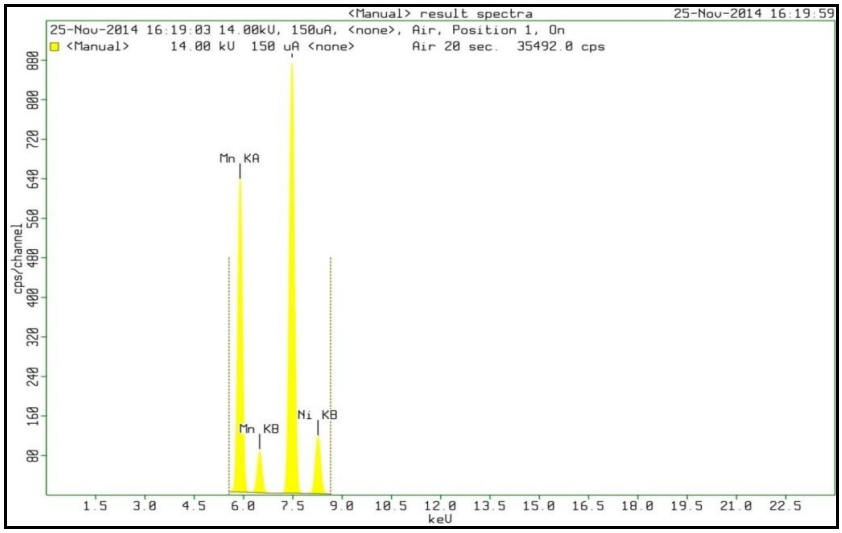

Fig.5b XRF Analysis for NiO/MnO nanocomposites.

Optical Analysis

UV-vis absorption spectra of NiO/MnO nano composites are shown in fig (6).The fig shows that the broad and less symmetric absorption peaks were observed at 420 nm, due to blue shifted as compared to the bulk material. The blue shifting of effects are caused due to the quantum size effect where as the broadening and assymmetricity are due to the huge size distribution of synthesized materials and it was also conformed to our SEM results[11].

The band gap energy (Eg) of the nano particles was calculated using the formula

$\alpha\, h\nu = B(\, h\nu - Eg)^{n}$,

Where n takes the value of ½ and 2 for direct and indirect transition respectively[12], *B* is a constant called band tailing parameter and hν is the incident photon energy. This absorption spectrum of chosen nanocomposite material gives the good relation between the particle and band gap obtain value of particle size is about5.5nm using the band gap of 4.1eVfor (420 nm) which is exactly coincide with the values obtained from XRD[13]. This may be attributed due to the charge transfer between the nanocomposite materials[14]. From the UV analysis we came to the conclusion that the band gap of a material increases when particle size of nanocomposites decreases[15].

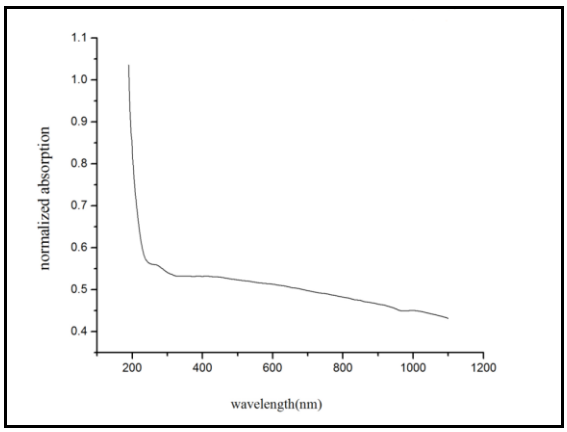

Fig.6 UV –Vis absorption spectrum for NiO/MnO nanocomposites

Conclusion

In this work, pure NiO, MnO nanoparticles and NiO/ MnO nanocomposites were successfully prepared using hydrothermal method. The XRD analysis confirmed the formation of orthorhombic phase MnO and cubic NiO. The particle size of nano particles were approximately 5-15 nm. The SEM analysis confirmed the rod

shape morphology of the NiO/MnO nano particles in the composite sample. From the UV-analysis we found that the band gap of NiO/MnO increased with decreasing particle size. The results are in good agreement with earlier work.

Acknowledgement

One of the authors (J.V.Swetha) sincerely thanks SRM University, Chennai for the award of carry SRM fellowship the research work. The authors gratefully acknowledge Prof. D. John Thiruvadigal, Head Department of Physics and Nanotechnology, SRM University for extending (DST-FIST) facilities to characterize the samples. The authors also thank Mr. C. Gopalakrishnan and Dr. Helen Annal Therese, Nanotechnology Research Centre, SRM University, Chennai for extending the facilities to record XRD pattern and SEM images.

References

1. kishore Sridharan , Nivya Roy ,Reji Philip,Tae Joo Park., Anomalous growth of multi- phased and multi-dimensional Manganese oxide–Metal (Fe, Co and Ni) oxide nanostructures, Synthesis and optical limiting properties, J. of Alloys and Compounds,2014 ,611 ,82–90.
2. Hugel J, Carabatos C., Band structure and optical properties of MnO, Solid State Communications, 1986,60, 369-372.
3. Gajendran j, Rajendran V., Synthesis and characterization of ultrafine SnO_2 nanoparticles via solvothermal process., Int.J. phy and app,2010, 2, 45-50.
4. Sujit Kumar Ghosha, Junjie Kanga, Makoto Inokuchi Naoki Toshimaa Solvent-mediated synthesis, characterization and electro catalytic activity o hydrophilic and dispersive Au–Mn3O4 nanocomposites, Applied Catalysis A: General,2013, 464–465, 225–232 .
5. Hui Zhang a,b, Hui-Jiuan Chen b, Xiaoze Du a, Photothermal conversion characteristics of gold nanoparticles Solar Energy, 2014 ,100, 141–147.
6. Jun Zang, Hang Qian, Zhikai Wei, Yong Cao, Mingsen Zheng∗, Quanfeng Dong Reduced Graphene Oxide Supported MnO Nanoparticles with Excellent Lithium Storage Performance. Electrochimica Acta , 2014, 118, 112–117.
7. Si-Dong Kim, Bum-Joon Kim, Jin-Ho Yoon and Jung-Sik Kim., Design, fabrication and characterization of a low-power Gas sensor with high sensitivity to CO gas, J korean phys. soc., 2007,51, 20692-076.
8. Abdullah G. Al-Sehemi , Ayed S. Al-Shihri , Abul Kalam , Gaohui Du , Tokeer Ahmad., Microwave synthesis, optical properties and surface area studies of NiO Nanoparticles, Journal of Molecular Structure, 2014, 1058, 56–61.
9. Yong Seung Jang1Jung Hyun Kim1 Jung-Kul Lee Byung Kyu Park Yun Chan Kang Electrochemical Properties of $0.6Li_2MnO_3{\cdot}0.4Li(Ni0.8Co0.15Al0.05)O_2$ Composite Nanopowders Prepared by Spray Pyrolysis Int. J. Electrochem. Sci, 2012,7,12370 – 12382.
10. Hui Qiao, Ning Wu, Fenglin Huang, Yibing Cai, Qufu Wei Solvothermal synthesis of NiO/C hybrid microspheres as Li-intercalation electrode material Materials Letters, 2010, 64, 1022–1024.
11. Alok Kumar Rai, Ly Tuan Anh, Chan-Jin Park, Jaekook Electroch Ceramics International chemical study of NiO nanoparticles electrode for application in rechargeable lithium-ion batteries. Ceramics International, 2013, 39, 6611–6618.
12. Byrappa K, Adschiri T., Hydrothermal technology for nanotechnology, Progress in Crystal Growth and Characterization of Materials, 2007,53 , 117-166.
13. Nowsath Rifaya M, Theivasanthi T, Alagar M., Chemical Capping Synthesis of Nickel Oxide Nanoparticles and their Characterizations Studies, Nanoscience and Nanotechnology, 2012, 2,134-138.
14. Fengdong Qu, Yongfan Wang, Juan Liu, Shanpeng Wen, Yu Chen, Shengping Ruan., Fe3O4–NiO core–shell composites: Hydrothermal synthesis and toluene sensing properties, Materials Letters, 2014, 132 ,167–170.
15. Guofang Du, Yongju Liu, Yuehuan Li, Kan Zhao, Heyun Zhao., Ultrasound-assisted synthesis of six-fold-symmetrical ZnO hierarchical architecture assembled by nanorods arrays Materials Letters, 2014, 137, 68–71.

*****