ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Hydrothermal Synthesis of MnO_2 Nanoparticles using Teflon Lined Autoclave

M Senthilkumar[a,b], Balamurugan[b]*, and BG Jeyaprakash[a,b]

[a]Centre for Nanotechnology & Advanced Biomaterials, [b]School of Electrical & Electronics Engineering, SASTRA University, Tamilnadu, Thanjavur -613 401, India

ABSTRACT

MnO_2 nanoparticles of different morphologyhave been synthesized by hydrothermal method using Teflon lined autoclave with cetyl trimethylammonium bromide (CTAB) as capping agent.The structure and morphology of the prepared MnO_2 were studied through X-ray diffraction, Scanning Electron Microscopy and Infrared Spectroscopy at room temperature.The influences of CTAB concentration on the morphology were analysed and reported.

Keywords: Teflon lined autoclave, CTAB, hydrothermal, MnO_2, nanoparticle

Corresponding author

INTRODUCTION

In recent years, nanoscale materials have proved to have uniqueproperties than its bulk due to large surface to volume ratio. Among many transition metal oxides, manganese oxide exhibits MnO, Mn_2O_3, Mn_3O_4, Mn_5O_8 and MnO_2forms. Of which, MnO_2 is the one of the most attractive oxide due to its unique properties. Manganese dioxide (MnO_2) is a low band gap, high optical constant semiconductor that exhibits ferroelectric and catalytic properties. It has wide applications, particularly as a reversible-cathode for lithium batteries [1,2], a catalyst for purification of air [3], in removal of CO from hydrogen rich fuel cell [4].

The manganese dioxide has octahedral [MnO_6] close packed structure, such that one manganese atom is co-originated with six oxygen atom in different ways and forms various crystallographic structure. Thus MnO_2 can exist in α, β, γand δstructural phase, of which, α-MnO_2 has been widely used in lithium based batteries. The properties of MnO_2 strongly depends onmicrostructure and hence on the processing condition. Different techniques have been reported to obtain MnO_2 nanoparticles, such as solid-state reaction [5], microemulsion [6], sonochemical [7] and hydrothermal method [8]. Surfactant mediated hydrothermal technique is one of the simplest techniquefor preparing reproducible size and shape of the nanocrystals. Also, the surfactant mediated route exhibit good crystallinity and monodispersity of nanoparticles [9-11].Huaihao Zhang [12] obtained hollow sphere of MnO_2 nanoparticle through surfactant-assisted co-precipitation method and reported the high specific capacitance of it. Hongju Li et al [13] enumerated the growth of α-MnO_2 nanotube from γ-MnO_2 in hydrothermal technique. Nian Tang et al [14] reported the formation of single crystalline α-MnO_2 nanorods in hydrothermal technique through redox reaction between MnO_4 and mixture of $KMnO_4$ and HNO_3.

In the present work, MnO_2 nanoparticle of different morphology was prepared using home built teflon lined autoclave unit. The effect of capping agent concentration on the morphology of the particle was studied.

EXPERIMENTAL

MnO_2 nanoparticles were preparedusing home built teflon lined autoclave unit. A0.2M of manganese acetate tetrahydradesolution was prepared in deionized water. To this, CTAB of desired concentrationis mixed and stirred for 30 minutes.Then 0.4M of sodium hydroxide solution was added under constant stirring. The resultant brown colour solution was then transferred into a Teflon lined stainless steel autoclave and maintained at 300^oC for 5 h. The resultant powder was centrifuged at 4000 rpm for 30 minutes and then annealed at 350^oC for 3 h. Similarly MnO_2 nanoparticles for different concentration of CTAB were prepared without varying the other parameter and are shown in table 1.The powders were thencharacterized by powder X-ray diffractrometer (XPERT-PRO, PW 3071) using Cu-Kα radiation, (FT-IR)(Spectrum100,PerkinElmer,USA)and Field emission scanning electron microscope (FESEM JEOL, JSM 6701).

Table 1: Preparation condition for differentMnO_2nanoparticle morphology

Manganese acetate tetrahytrate	Sodium hydroxide	Cetyltrimethyl ammonium bromide	Temperature	Pressure	Volume	Morphology
0.2 M	0.4 M	0.0003 M	300˚C	50 bar	30 ml	Nanosphere
0.2 M	0.4 M	0.003 M	300˚C	50 bar	30 ml	mixed sphere and rod
0.2 M	0.4 M	0.03 M	300˚C	50 bar	30 ml	Nanorod

RESULT AND DISCUSSIONS

Structural Analysis

Fig. 1shows the X-ray diffraction pattern of prepared powders. The XRD pattern exhibited peaks at 18˚, 28˚, 31˚, 36.09˚, 38˚, 44.41˚, 50.7˚, 59.88˚ and 64.70˚ indicating the formation of tetragonal α-MnO_2. The peaks were indexed to (200), (310), (101), (211), (301), (411), (521), (002) and (541) planes with respect to JCPDS 44-0141.No impurity peaks such as other phase of manganese oxide and elements were found in the x-ray diffraction pattern, indicating the formation of pure α-MnO_2 particles. The (211) plane was found to have high intense followed by (101) and (310). The presence of different oriented peaks indicates the polycrystalline nature of the particle. Also, all the peaks found to be broadened and indicating the formation of small crystallites. The crystallite size was estimated using Scherer formula.

$$D = \frac{K\lambda}{\beta \, Cos\, \theta}$$

Where D is the crystallitesize, Kis the shape factor, λ the X-ray wavelength, θ the Bragg's angle in radians, and β the full width at half maximum in radians. The crystallite size obtained from the preferentially oriented peak of (211) plane was found to be 30nm.

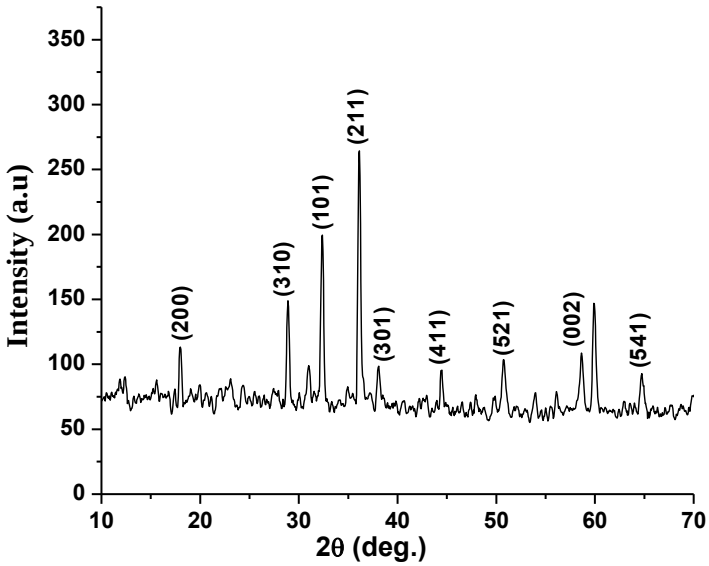

Fig. 1 XRD pattern of α-MnO_2nanoparticle

FTIR Studies

Fig. 2 shows the FTIR spectrum of prepared MnO_2 particle. The bands around 3398.36 and 1734.12 cm^{-1} corresponds to O-H vibrating mode and is due to physically adsorbed water on MnO_2 crystalfrom the environment. Thebands between 610.54 and 510.65 cm^{-1} is the characteristic peak of MnO_6 octahedron of MnO_2 [15-17]. No significant change was observed in the FT-IR spectrum of MnO_2 particles obtained from different CTAB concentration. Also the spectrum does not show other organic groups found in the precursor solution.

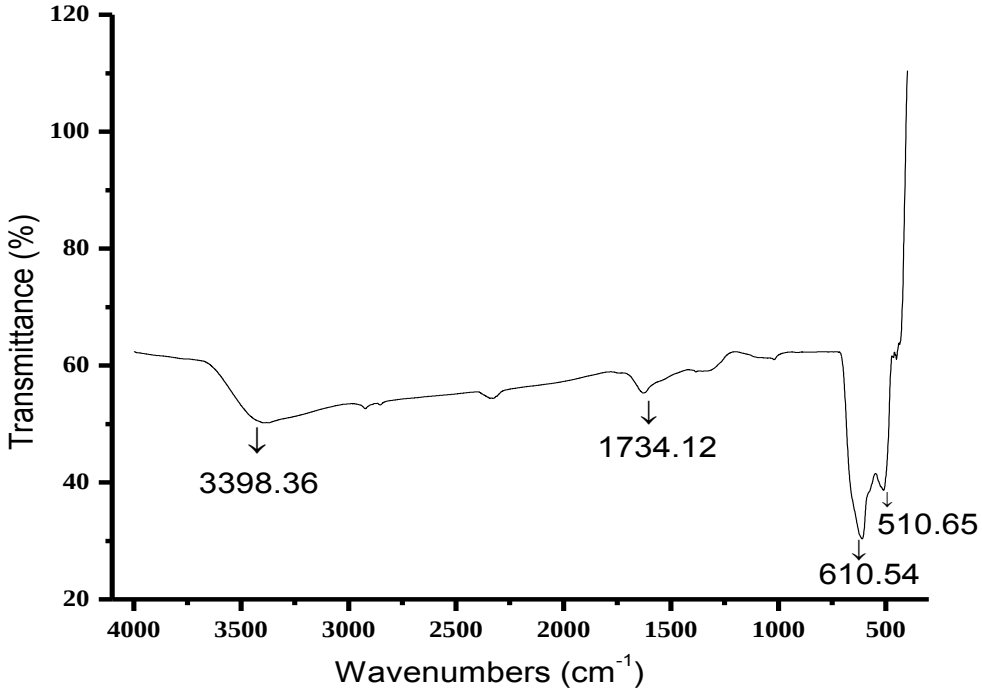

Fig. 2 FTIR spectra of as prepared MnO_2 nanoparticle

FE-SEM Studies

Fig. 3(a-d) shows the FE-SEM of synthesized MnO_2powder. Fig. 3(a) indicates the formation of spherical shape particle with size lying between 25 and 40 nm. The observed crystallite sizes also aggress with the XRD result. As the concentration of CTAB increases to 0.03M, the morphology changes to mixed sphereand rod (Fig. 3b). Further increase in concentration to 0.3M shows the formation of rods (Fig. 3d). These changes in morphology can be attributed to micelle formation [18] of capping agent. However further studies is required to analysis the growth of MnO_2 nanoparticles in surfactant environment.

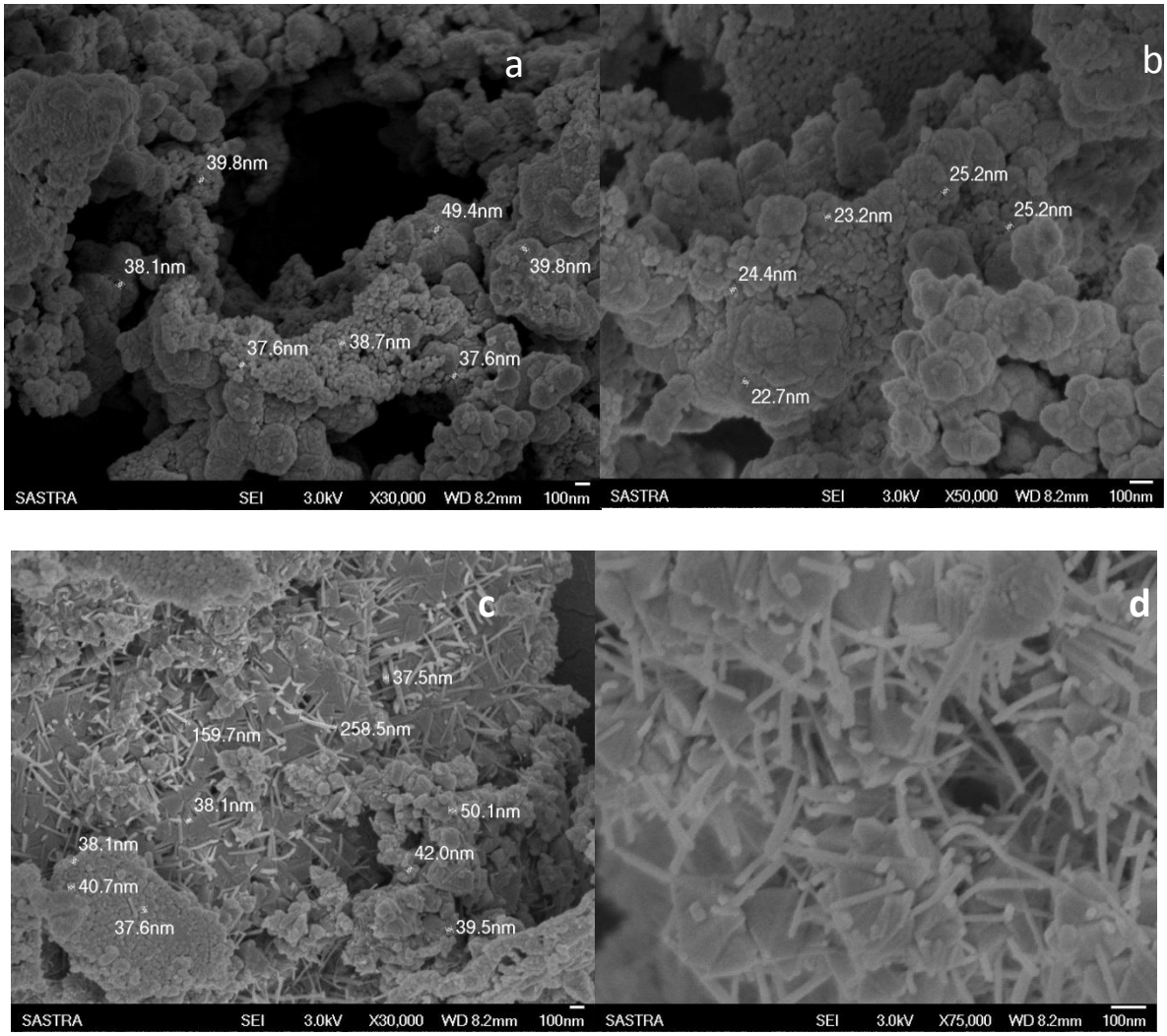

Fig. 3 FESEM of MnO_2 nanoparticles prepared from different CTAB concentration

CONCLUSION

MnO_2 nanoparticles have been successfully synthesized by hydrothermal method using teflon lined autoclave with CTAB as capping agent.X-ray diffraction pattern indicates the formation of α-MnO_2 phase with polycrystalline nature andthe preferential orientation was found to be (211) plane. FESEM shows the formation of spherical, mixed spherical-rodand rod like morphology as CTAB concentration increases.

REFERENCES

[1] Shao-Horn Y, Hackney SA, Johnson CS, Thackeray MM. J Electrochem Soc 1998;145; 582-589.
[2] Zoltowski P, Drazic DM, Vorkapic L. J Appl Electrochem 1993; 3: 271-283.
[3] Jiang B, Liu Y, Wu Z. J Hazard Mater2009; 146: 1249.
[4] Zwinkels MFM, Jaras SG, Menon PG, Griffik TA. Catal Rev Sci Eng 1993; 35; 319-358.
[5] YuanA,Wang X, Wang Y, Hu J. Electrochimica Acta 2009;54(3):1021–1026.

[6] Xu C, LiB, Du H, Kang F,ZengY. J Power Sources 2008;180: 664–670.
[7] Zolfaghari A, Ataherian F, Ghaemi G, Gholami A. Electrochimica Acta 2007;52:2806–2814.
[8] Yan D, Yan P, Cheng S. Crystal Growth and Design 2009; 9:218–222.
[9] Zhang Z, Sun H, Shao X, Li D, Yu H, Han H. Adv Mater 2005;17: 42–47.
[10] Tang Z, Kotov NA, Giersig M. Science 2002;297: 237–240.
[11] Hou Y,Kondoh H, Ohta T, Gao S. Appl Surf Sci 2005;241:218–222.
[12] Huaihao Zhang, Yaqiong Wang, Changwei Liu, Haitao Jiang. J Alloys Compd 2012; 517:1– 8.
[13] Hongju Li, Wen-lou Wang Fangfang Pan, Xiaodong Xin, Qinqin Chang, Xianming Liu. Mater Sci Eng B 2011;176:1054– 1057.
[14] Nian Tang, XikeTian, Chao Yang, Zhenbang Pi, Qing Han. J Phys Chem Solids 2010;71: 258–262.
[15] Fang DL, Wu BC, Mao AQ, Yan Y, Zheng CH. J Alloys Compd 2010;507:526.
[16] Ai ZH, Zhang LZ, Kong FH, Liu H, Xing WT, Qiu JR. Mater Chem Phys 2008; 162-167.
[17] Ananth MV, Pethkar S, Dakshinamurthi K. J Power Sources 1998;75:278-282.
[18] Chandrasekaran P, Viruthagiri G, Srinivasan N. J Alloys Compd 2012;540:89-93/