



Preparation of MnO₂ from manganese natural ore

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Abstract: Owing to wide applications of manganese oxides in waste water treatment, fertilizers, catalysis, sensors, super capacitors and rechargeable batteries has got novel attention worldwide. Natural ore of manganese were crushed manually and heated to dissolve in concentrated HCl. This solution was treated with potassium ferrocyanide to remove iron and other metallic unwanted particles. The precipitated powder was treated with potassium hydroxide to separate out manganese. Compound formation of MnO₂ powder is confirmed using FTIR, XRD. Microstructure is characterized using SEM technique. Band gap is determined using UV-visible spectroscopy. Compound formation, grain size and surface characteristics before and after treatment are discussed in this paper. Further improvement towards the formation of nanoparticles is in progress.

Keywords: MnO₂, nanoparticles, grain size, band gap.

1 Introduction: Manganese oxide nanoparticles of size less than 100 nm have received increasing interests owing to their potential applications in the field of dry cell battery, zinc carbon battery, magnetic and catalytic properties. It is possible to use α -MnO₂ as a cathode for lithium ion batteries. After iron oxide, now these days, nanoparticles of metals like Al, Zn, Ti and Mn oxides have found tremendous applications in the development of Science and Technology. Before any application of nanoparticles, one must think of health and environmental issue. Nanoparticles could be inhaled, swallowed, absorbed even through our skin. It can trigger inflammation and weaken the immune system. It can also interfere with regulatory mechanism of enzymes and proteins. However there is no potential risk of Mn nanoparticles as Mn is an essential element of plants. Particularly, MnO and MnO₂ nanomaterials have electrical, magnetic and catalytic properties such as anode materials in lithium-ion batteries which are having high capacity at low cost [1-3]. Manganese nanoparticles (MnO₂NP) work as a better micronutrient than commercially available manganese salt. It is also known that phase, shape, size, and dimension of the particles greatly influence the properties of the nanomaterials [4]. Many efforts are being made to prepare MnO₂ nanoparticles using hydrothermal method [5], sol-gel method [6], wet chemical route [7], pulsed laser deposition method [8] and precursor techniques [9]. Lots of successes on the properties and applications of manganese oxide nanomaterials have been achieved in the last few years, for example, a hydrothermal method has been used to synthesize sea urchin shaped α -MnO₂ [10]. Wu et al. have prepared γ -MnO₂ hexagon-based layer-cake-like and intertexture-like nano-architectures via a hydrothermal route [11]. Liu and coworkers have found MnO₂ nanoparticle-enriched poly(3,4-ethylenedioxythiophene) nanowires that could maintain high specific capacitance at high charge-discharge rates [12]. Their characteristics are studied using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray diffraction (XRD), Fourier Transform Infra-red Spectroscopy (FTIR) and UV-visible spectroscopy.

Different types of manganese ore are present in the earth crust. Manganese is not found in pure state in earth crust. It is available in compound form with other metals like iron and minerals. There is variety of manganese bearing minerals. Very less effort has been made to prepare its nanoparticles. We report the preparation of MnO_2 compounds from its natural ore collected from Tata Steel Ltd., Jamshedpur using Sol-gel method. Compound formation of MnO_2 is confirmed using fourier transform infra-red spectroscopy (FTIR) and X-ray diffraction (XRD) techniques. SEM is used to investigate the microstructure. UV-Visible spectroscopy is used to determine the band gap of the prepared MnO_2 powder.

2. Materials and methods:

2.1.1 Chemicals: Manganese ore is collected from Tata Steel Ltd. Jamshedpur for research purpose. It is in concrete form which is very hard (Figure 1). The chemical composition of this ore were 30.70 % Mn, 25.7 % Fe, 2.48 % silica, 5.30 % alumina and 0.01 % phosphorous (all weight %) as provided by the supplier. Concentrated HCl is used to digest the Manganese ore.

2.1.2 Preparation of sample: Pristine ore of Mn were not getting dissolved in concentrated acid. Therefore, it was heated at 600 °C in air atmosphere. After that it was crushed manually and put in concentrated HCl. It didn't dissolved in concentrated HCl. However when samples were heated at 900 C, it got dissolved. Samples were crushed to mm size or even less. To remove the other metallic ions, the solution was treated with potassium ferrocynide which forms complexes of manganese. The precipitate was treated with potassium hydroxide to separate out manganese oxide. Hereafter, this will be referred as sample in the manuscript.



Figure (1): Photograph of the manganese ore as procured from Tata Steel Ltd., India.

2.2 Analysis and characterization:

2.2.1 Instruments: Functional group present in the MnO_2 nanoparticles were identified using FTIR (Shimadzu, Japan, IR-Prestige 21) where the measurement were carried out in the mid-infrared range (400 - 4000 cm^{-1}). The XRD (INEL XRG -3000 X-ray diffractometer) patterns were recorded using $\text{CuK}_{\alpha 1}$ radiation ($\lambda = 1.54056 \text{ \AA}$) generated at 40 kV and 30 mA. The surface morphology of MnO_2 nanoparticles were studied by scanning electron microscopy (SEM, JEOL, Japan, JSM6390LV). Band

gap of the MnO_2 nanoparticles were studied using UV-Visible spectroscopy (Perkin-Elmer, Lambda-20) at BIT Mesra, Ranchi.

2.2.2 Fourier transform infrared (FTIR) spectroscopy analysis: Mn-O bond vibrational modes were determined using FTIR technique. Functional groups present in the sample were identified using FTIR in the mid-infrared range ($400 - 4000 \text{ cm}^{-1}$).

2.2.3 X-ray diffraction (XRD) analysis: The powder XRD was carried out at IGCAR Kalpakkam. $\text{CuK}_{\alpha 1}$ radiation of wavelength 1.54 \AA was used to record the spectra. Grain size of the each peak was determined using Scherrer's formula [13].

2.2.4 Scanning electron microscopy (SEM) and UV-Visible spectroscopy analysis: The surface morphology of the MnO_2 nanoparticles was observed using scanning electron microscopy at BIT Mesra Ranchi. Band gap of the MnO_2 nanoparticles was studied using UV-visible spectroscopy at BIT Mesra, Ranchi.

3. Results and discussion:

3.1 FTIR analysis: Infrared spectra of the ore, roasted ore and MnO_2 nanoparticles are shown in the Fig. 2. The bands at 447 , 432 , 420 and 390 cm^{-1} correspond to the Mn-O bonds confirming the formation manganese oxides. These vibration modes were not observed in the pristine ore and roasted ore.

3.2

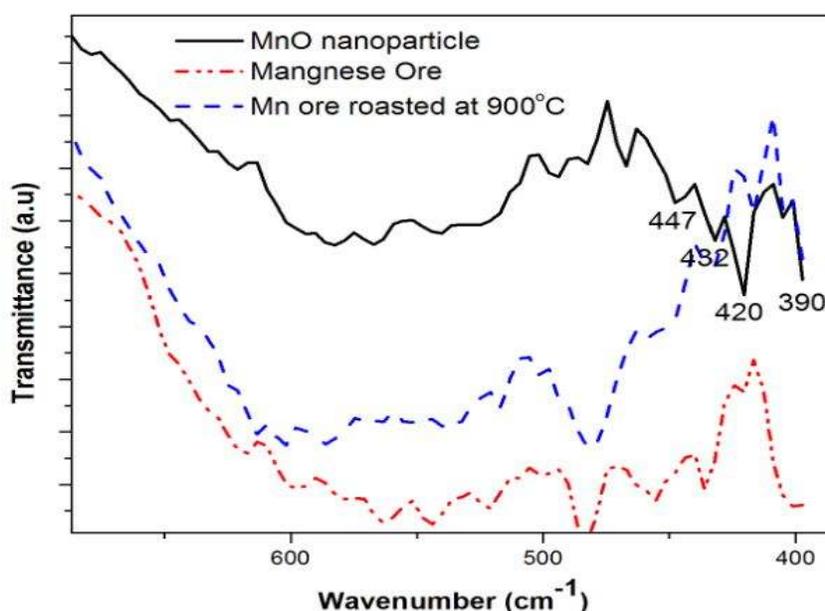


Figure (2): FTIR spectra of the pristine ore, roasted ore and MnO_2 nanoparticles showing the Mn-O vibrational modes in the nanoparticles.

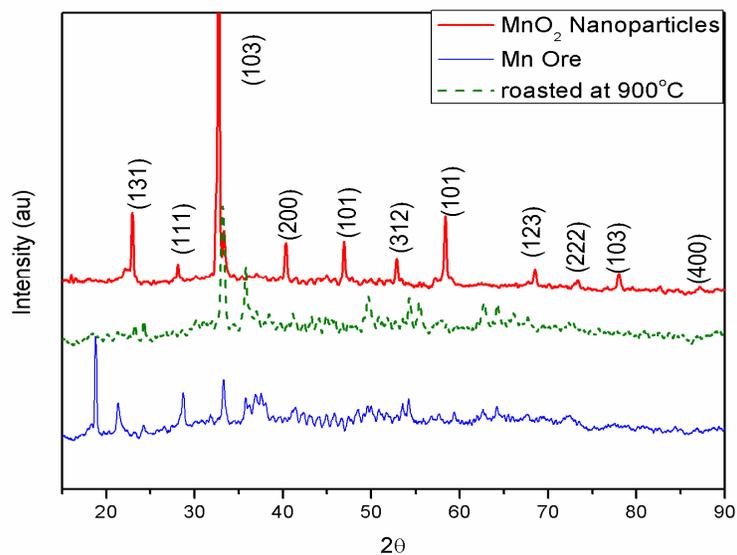


Figure (3): XRD plot of pristine ore, roasted ore at 900 °C and of MnO₂.

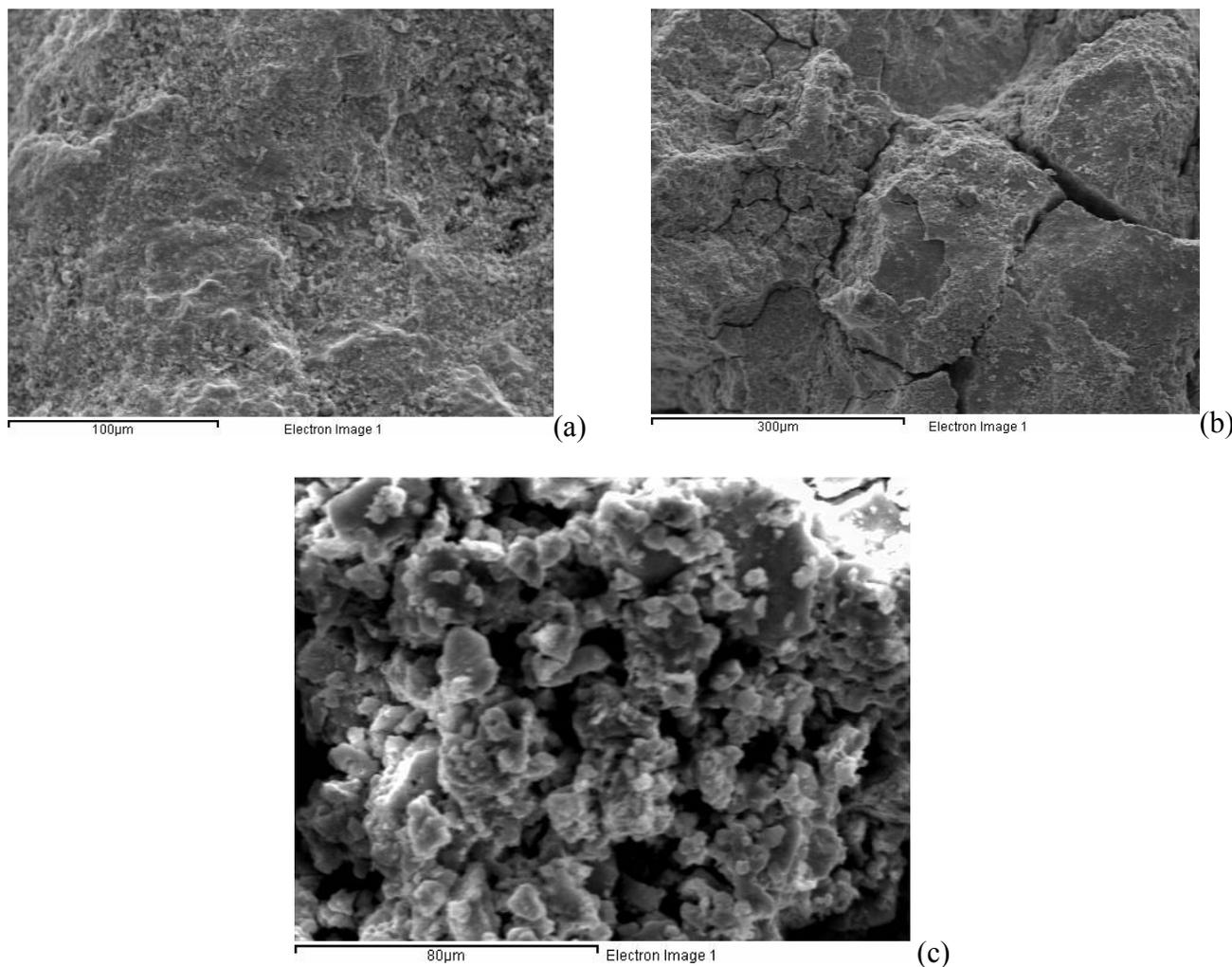


Figure (4): (a) SEM image of manganese pure ore (b) manganese roasted ore (c) formed MnO₂.

3.2 X-ray diffraction studies: Figure (3) shows the compound present in the pure ore, roasted ore and prepared nanoparticles together. Crystalline phases of Mn, Fe, Si and Al were observed in the pure ore and in the roasted samples. New peaks of crystalline manganese oxides of different phases are seen after chemical treatment. All the phases of MnO_2 are indexed. Average crystallite size is of the order of 50 - 100 nm as estimated by Scherrer formula.

3.3 SEM analysis: Figure (4a) shows the SEM image of manganese pure ore. Figure (4b) shows the roasted sample. Figure (4c) shows the SEM image of prepared MnO_2 after chemical treatment. Clearly size becomes much smaller than observed for pristine and roasted ore. EDX spectra show the presence Cl after chemical treatment in addition of Mn which has to be removed. Further modification is in progress.

3.4 UV-Visible analysis of MnO_2 nanoparticles: This technique is used to determine the band gap of the semiconductor or dielectric materials [14]. The term ‘band gap’ refers to the energy difference between the top of the valence band to the bottom of the conduction band. Figure (5) shows the UV visible spectrum of the MnO_2 nanoparticles. From the slope of the curve the minimum absorbance, i.e., strong cut off is observed at 430 nm wavelength which corresponds to 2.90 eV band gap. This corresponds to UV-visible region of the electromagnetic spectrum.

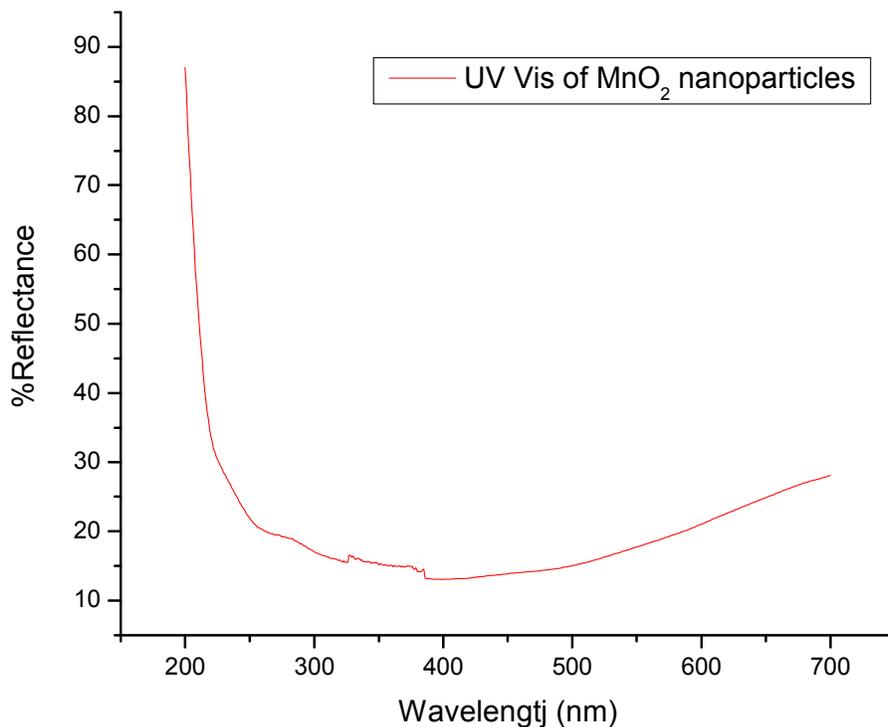


Figure (5): UV-Vis spectra of MnO_2 nanoparticles

4. Conclusions: MnO_2 powders of micron sizes are prepared using chemical method successfully. Compound formation of MnO_2 is confirmed using XRD and FTIR techniques. Microstructure is observed using SEM. Band gap of the MnO_2 is determined using UV-Vis spectroscopy. Band gap lies in the region of visible spectrum which implies that this can also be used as energy materials.

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