Rietveld refinement and experimental determination of optical and electrical properties of K$^+$ stabilized $\alpha$-MnO$_2$ nanostructures

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Abstract. In the midst of strenuous efforts in fabricating materials for supercapacitors, lithium ion batteries, molecular sieves and catalysts, manganese dioxide plays a vital role due to their unique tunnel framework. Alpha phased manganese dioxide ($\alpha$-MnO$_2$) nanoparticles are synthesized using a low temperature coprecipitation method. The structural and morphological characterization carried out by XRD, SEM and HRTEM techniques, confirms the formation of $\alpha$-MnO$_2$ nanoparticles. The EDS results confirmed the non stoichiometry and the presence of K$^+$ ions within the crystal lattice. The non stoichiometry is due to the large number of oxygen vacancies within the crystal. Rietveld refinement of XRD pattern was carried out to study in detail the role of K$^+$ ions in maintaining the stability of the 2x2 tunnel framework of $\alpha$-MnO$_2$. The UV-Vis absorption and photoluminescence spectrum were studied for analyzing the energy band structure of MnO$_2$. A direct band gap of 1.66 eV is obtained from the famous Taucs plot. The photoluminescence exhibits strong emission line in the visible region at 743 nm and defect related emission peaks at 757 and 751 nm. The dielectric studies were carried out using dielectric spectroscopy. The temperature dependence of orientation polarization can be understood from the study of variation of dielectric constant and losses with temperature. Moreover, the phase purity of the sample and the Mn-O vibrational frequencies were analyzed using FTIR spectrum.

1. Introduction

Manganese dioxide (MnO$_2$) is an important transition metal oxide which shows versatile properties due to their variable oxidation states. The different polymorphic states of MnO$_2$ arise due to the difference the structural arrangement of the basic MnO$_6$ octahedra. Among the different polymorphic states alpha phased MnO$_2$ ($\alpha$-MnO$_2$) consists of a 2x2 and 1x1 tunnel structure formed by corner sharing and edge sharing of MnO$_6$ octahedra. This unique structure is useful in lithium ion batteries and molecular sieves which can be applied to areas like long lasting battery technology and water harvesting technology. Various approaches have been used to fabricate manganese dioxide, such as self-reacting microemulsion [1], precipitation [2], room-temperature solid reaction [3], sonochemical [4], hydrothermal methods [5-8]
and co-precipitation [9]. In the present work alpha phased MnO₂ (α-MnO₂) nanoparticles were synthesized using a coprecipitation method. Here in order to study the role of K⁺ ions in maintaining the structural framework of the tunnel structure refinement was done with and without K⁺ ions.

2. Experimental section

Potassium permanganate (98.5 %, E. Merck), and Manganese Nitrate (99 %, E. Merck) were used as received without further purification. Ultra-pure water was used for the preparation of all reagents solutions. Manganese Nitrate (Mn(NO₃)₂) and Potassium Permanganate (KMnO₄) were first dissolved in distilled water the appropriate molar ratio. The solution was heated at 60°C for 3hrs with continuous stirring. The products were washed and dried. The sample were annealed at 70°C for 3hrs.

The X-ray diffraction (XRD) patterns were collected with a Bruker AXS D8 advance X-ray powder diffractometer equipped with a scintillation counter using Cu Kα radiation (λ = 1.5406Å²). Energy dispersive spectrum (EDS) spectrum was obtained from JEOL Model JED – 2300 instrument. Transmission electron microscopy (TEM) was carried out on a JEM-2100 transmission electron microscope operated at an accelerating voltage of 60-200 KV in 50 V steps. The band gap studies were carried out by a UV-Vis spectrometer (Varian, Cary 5000). The Fourier transform infrared spectroscopy (FTIR) and photoluminescence (PL) studies were done using Thermo Nicolet, Avatar and Perkin Elmer LS 45 spectrometers.

3. Results and discussion

The phase and purity of the products are first examined by XRD. Figure 1 shows the refined XRD pattern along with the crystal structure with and without potassium in the lattice. All the peaks in the XRD pattern can be indexed to a pure body-centered tetragonal α-MnO₂ phase, with lattice constants of a = 9.72 Å, c = 2.86Åⁿ, which are in agreement with the standard values of JCPDS 44-0141. With the aid of the famous Scherrer formula the average particle size of the nanoparticles are found to be 24 nm. Absence of additional peaks of other phases indicates the phase purity of the final product. The Rietveld refinement is carried out for a tetragonal unit cell having space group I 4/m using pseudo Voigt function. In MnO₂ Mn is associated with Wyckoff position 8h, oxygen at 8h and K⁺ ions at 2b. Refined unit cell parameters comes out to be a = 9.8165 Å and c = 2.8557Å. A detailed study of the crystal structures are required so as to analyze the importance of K⁺ ions in maintaining the structural framework of α-MnO₂ [10]. The structural framework consists of basic MnO₆ octahedra in an edge shared and corner shared fashion resulting in a (2x2) + (1x1) tunnel structure. It is the size of the tunnel that is capable of accommodating a K⁺ ion for structural stability. The potassium ions are distributed throughout the crystal structure. The crystal structure obtained incorporating K⁺ ions with the refinement parameters matches well with the reported cryptomelane architecture [10]. The 2 x 2 tunnel structure is capable of incorporating a K⁺ ion, whereas for the refinement procedure done without K⁺ ions the tunnel framework is completely disfigured. Also a collapse of the basic MnO₆ octahedra which is the building block of the tunnel framework is observed. Hence the K⁺ ions which gets intercalated to the 2 x 2 tunnel space of the crystal structure is capable of holding the tunnel framework. To gain better understanding of the nanoparticles, SEM and HRTEM images (Figure 2) of the sample is necessary. The SEM image clearly reveals that the synthesized nanoparticles have no defect or dislocation and also they are single crystalline. The particles obtained from HRTEM shows that the particle has a size distribution in the range 19nm – 35nm. These results are in good agreement with XRD result.
Figure 1. Rietveld refined XRD pattern of (a) without K$^+$ ions (b) with K$^+$ ions. Crystal structure of prepared sample (c) without K$^+$ ions (d) with K$^+$ ions

The compositional constituency of the prepared sample can be analysed using Energy dispersive spectroscopy (EDS). The EDS spectra (Figure 3 (a)), confirms the presence of Mn, O and K in the sample. The potassium ions stabilize the tunnel framework of the crystal structure. From the analysis it was found that the MnO$_2$ nanoparticles are nonstoichiometric with a large number of oxygen vacancies. This results in an mixed oxidation state of Mn throughout the sample. Diffuse reflectance spectral studies in the UV-Vis region were used to estimate the optical band gap of the synthesized nanorods. The calculated band gap from the Tauc plot is 1.68 eV and is higher than the reported values for nanostructured MnO$_2$ [11]. This high value may be attributed to better quantum confinement effect of MnO$_2$. Figure 3 (c) shows the PL spectra of MnO$_2$ nanoparticles with an excitation wavelength of 500 nm. As indicated in the figure the spectrum exhibits prominent emission bands with peaks at 1.66 (743 nm), 1.65 (751 nm) and 1.63 eV (757 nm).

The intense emission peak at 1.66 eV corresponds to the band edge emission. The peak at 1.63 eV may be assigned to the oxygen vacancy related defects. MnO$_2$ being a highly non stoichiometric material, is rich in oxygen vacancies. The EDS result also confirms the presence of oxygen vacancies. A weak peak at 1.65 eV may be assigned to the surface dangling bonds or surface defects. The phase purity of the sample can be analyzed using FTIR spectrum (Figure 3 (d)). The bands around 3407, 1602 cm$^{-1}$ and 1116 cm$^{-1}$ corresponds to the O-H vibration mode of traces of adsorbed water .The peak at 511 cm$^{-1}$ is due to
Figure 2. (a) SEM images and (b) HRTEM images of synthesised MnO$_2$ nanoparticles.

Figure 3. (a) EDS spectrum (b) Tauc plot (c) pl spectrum and (d) FTIR spectrum of $\alpha$-MnO$_2$ nanoparticles.
displacement of oxygen anions relative to Mn cation along the direction of octahedron chain, or we can say it is due to metal-oxygen (Mn-O) bending vibrations of [MnO₆] octahedral in α-MnO₂ nanoparticles.

The net polarisability of a composite depends on several components namely, electronic, atomic, interfacial and orientation polarisability. All these contribute towards the dielectric constant of a given material. Only orientation polarisability depends directly on temperature. Figure 3 shows the variation of dielectric constant and dielectric loss with temperature. As the temperature increases the dielectric constant increases to a very high value at 80°C and then the values start to decrease. When an electric field is applied on a polar material, the potential energy of the associated dipoles change. The orientations aligned with the field will have a lower potential energy compared to that of the orientations aligned against the field. Less amount of energy is required to get aligned with the applied electric field and more energy is required to get aligned the applied field.

![Graph](image)

Figure 4. Variation of (a) dielectric constant and (b) dielectric loss with temperature.

At room temperature conditions, only some of the molecules will have the required energy to align themselves with the applied field. On increasing the temperature from 30°C to 80°C the energy in the system is enough to increase the potential energy of the remaining orientations to that critical value where they get themselves aligned with the applied electric field resulting in a high net orientation polarization and hence an increase in dielectric constant values is observed.

On increasing temperature further above 80°C, the dielectric constant values decreases. This is due to the reason that as temperature increases to higher values, the molecular vibrations of the molecules increases along with random thermal motion to such an extent that, the range of deviation from aligning itself to the applied electric field increases resulting in molecules less closely aligned to themselves and applied electric field (Figure 4).
Figure 5. Effect of temperature on orientation polarization

As temperature increases further the energy of the orientations becomes close to the critical potential energy required to align the dipoles or molecules against the applied electric field. Above all mentioned factors contribute to a decrease in net orientation polarisability and hence the dielectric constant values decreases. The same trend is seen in the case of loss factor also. As temperature increases the loss factor increases up to a particular temperature and then starts to decrease. The increase in frequency causes a lag in orientation polarization which in turn results in lowering of the dielectric constant. From the graph it is obvious that at MHz frequency range the value of dielectric constant and dielectric loss of MnO$_2$ nanoparticles becomes independent of temperature.

4. Conclusion

Manganese dioxide nanoparticles are synthesized using a coprecipitation technique. The XRD pattern and Rietveld refinement confirms the phase and the crystal structure formed. The morphology of the sample and material composition has been identified by HRTEM and EDS, respectively. The role of K$^+$ ions in maintaining the 2 x 2 tunnel framework is studied in detail. The band gap of the sample is found to be 1.68 eV larger than the reported values, which is due to quantum confinement effects. The photoluminescence spectrum throws light on the band structure of α-MnO$_2$ nanoparticles. The intense emission peak at 1.66 eV corresponds to the band edge emission. The peak at 1.63 eV may be assigned to the oxygen vacancy related defects. A weak peak at 1.65 eV may be assigned to the surface dangling bonds or surface defects due to Mn interstitials. As temperature increases the dielectric constant increases and then decreases after attaining a particular temperature. The increase is due to the increase in mobility of permanent dipoles which leads to orientation polarization.

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