Synthesis and Study on Structural, Morphological and Magnetic properties of nanocrystalline Manganese Oxide

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Abstract: Mn$_2$O$_3$ nanoparticles were prepared by co-precipitation method followed by annealing of samples at 300 °C for 2 hours. The samples were characterized to find the structural, functional, optical, morphological, compositional and magnetic properties by PXRD, FTIR, Micro-Raman, HRSEM, TEM, XPS, EDX and VSM respectively. Structural studies by PXRD indicate that the annealing has strongly influenced the phase transition showing two coexisting phases of Mn$_2$O$_3$ and Mn$_3$O$_4$. Micro-Raman spectra showed the presence of A$_{1g}$ mode of vibration corresponding to Mn$_3$O$_4$ phase. Magnetic studies of the as synthesized Mn$_2$O$_3$ nanoparticles depict paramagnetic behavior at room temperature.

Keywords: manganese oxide, co precipitation, magnetic properties

1. INTRODUCTION

In recent past, considerable research attention is paid on Mn based compounds as it has many interesting properties that can be tailored for numerous applications. Mn$_2$O$_3$ is an important transition metal oxide due to its extensive applications in magnetic [1], electrochemical [2], Li ion batteries [3], catalytic applications [4], supercapacitors [5] and dilute magnetic semiconductor [6]. Mn$_2$O$_3$ nanoparticles have been synthesized in several methods like hydrothermal [7], combustion method [8], microwave assisted solution method [9], and co precipitation method [10]. In this report, we have attempted to optimize Mn$_2$O$_3$ nanoparticles by facile co-precipitation method as it is simple and cost effective technique. As synthesized nanoparticles were annealed to 300 °C and their structural, morphological, functional, compositional and magnetic properties were compared.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of Manganese Oxide Nanoparticles

All chemicals used were of AR grade and was used without further purification. A simple chemical co precipitation method was employed to synthesize Mn$_2$O$_3$ nanoparticles. 1M of MnSO$_4$·H$_2$O was dissolved in de-ionized water. 2M of NaOH was added drop wise to this solution and pH was maintained at 11±0.2 by adding ammonia. Solution was stirred continuously under constant temperature (60 °C) for 2 hours for precipitation of nanoparticles. Then precipitated particles was collected and washed with de-ionized water 2 to 3 times and dried in hot air oven at 100 °C for 12 hours. As synthesized particles was annealed at 300 °C for 2 hours.

3. RESULTS AND DISCUSSION

3.1 Structural Studies

Figure 1 show the powder X-ray diffractograms of as synthesized and annealed nanoparticles, which reveals the presence of mixed phases of Mn$_2$O$_3$ and Mn$_3$O$_4$. PXRD pattern of as synthesized nanoparticles show predominant peak with reflection (311) at 34.06° which indicates the presence of Mn$_2$O$_3$ phase with cubic structure, whereas annealed sample shows predominant peak with reflection (222) at 32.45° which can be assigned to Mn$_3$O$_4$ phase with cubic structure. The reflections (222) at 36.06° and (440) at 60.24° can be assigned to Mn$_3$O$_4$ phase. These values are in good agreement with JCPDS card # 040-732. The peaks with reflection (200) at 19°, (220) at 29°, (222) at 32.45°, (400) at 37.9°, (332) at 44.52° and (600) at 58.29° belongs to Mn$_2$O$_3$ phase with cubic structure. These peaks are well matched with JCPDS card # 89-4836. Aroused peak intensity of annealed nanoparticles is due to the increase in crystallinity. Due to annealing, there is shift in peak to (222) which is the crystallographic plane indicating the phase change to Mn$_3$O$_4$ and this may be due to oxidation of Mn$_2$O$_3$ to Mn$_3$O$_4$ begins at as low as temperature at 300°C [11-12].

![Figure 1. PXRD diffractograms of as synthesized and annealed mixed phases of Mn$_2$O$_3$ nanoparticles.](image-url)
states data at surface of the samples. Inset picture shows narrow window scan of Mn 2p state. The survey spectrum shows the presence of Mn, C and O with the presence of no other impurities. The C 1s (284.5 eV) peak was used for the calibration of the spectrum as internal reference. Electronic states of Mn 3s, O 1s, Mn 2p and Mn 3p are well matched with earlier reported values [2]. The peak at 642.7 eV can be assigned to Mn 2p_{3/2} corresponding to Mn 3^+ and 48 eV can be assigned to 3p_{3/2} electronic state [14]. Spin orbit splitting between Mn 3p_{3/2} and Mn 2p_{3/2} is 11.8 eV which is nearer to literature reports [7]. The binding energies at the Mn 2p_{3/2} and Mn 2p_{1/2} peaks agree well with that of reported for MnO_{4} indicating oxidation state for Mn [5]. Figure 3 (a&b) shows EDX spectra of as synthesized and annealed nanoparticles. It indicates the presence of Mn and O with the presence of no other impurities.

Table 1. Lattice parameters of as synthesized and annealed MnO_{4} nanoparticles

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter (Å)</th>
<th>Volume (Å³)</th>
<th>lattice distortion n(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-synthesized</td>
<td>8.7566</td>
<td>671.428</td>
<td>12.92</td>
</tr>
<tr>
<td>Annealed</td>
<td>8.7887</td>
<td>678.850</td>
<td>20.35</td>
</tr>
</tbody>
</table>

Table 2. Microstructural parameters of as synthesized and annealed MnO_{4} nanoparticles

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crystallite size (nm)</th>
<th>Dislocation density(10^{15} lines/m²)</th>
<th>Micro strain (lines^{-2} m^{-3})</th>
<th>Micro strain (lines^{-2} m^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>As synthesized</td>
<td>31.7</td>
<td>0.996</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td>91.6</td>
<td>0.119</td>
<td>0.0004</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2 XPS spectrum of as synthesized MnO_{4} nanoparticles. Inset

Figure 3 EDS spectra of (a) as synthesized and (b) annealed MnO_{4} nanoparticles

3.3 Functional Studies

The Raman scattering measurements were performed using the 514.5nm excitation line from Ar⁺ laser. Figure 4 (a&b) shows the micro-Raman spectra of as synthesized and annealed nanoparticles respectively. As synthesized nanoparticles exhibits three phonon peaks at (doubly degenerate) T_{2g} symmetry mode at 366 cm⁻¹, E_{g} symmetry mode at 320 cm⁻¹ and a single degenerate A_{1g} symmetry mode at 654 cm⁻¹. The band corresponding to 654 cm⁻¹ is very close to 655 cm⁻¹ which is due to the stretching vibration of Mn-O in MnO_{4} [7]. Annealed nanoparticles shows four phonon peaks same as synthesized particles with one extra band T^{1g} symmetry mode at 487 cm⁻¹ which may be due to the out of plane bending mode of MnO_{4} phase. Presence of mixed phase of MnO_{2} and MnO_{4} is confirmed from these peaks. Also peak intensity of annealed nanoparticles is lesser than that of as synthesized particles. This may be due to increase in crystallite size for annealed nanoparticles which can be explained using phonon confinement effect as reported earlier by Jian Zuo et al [27].

Figure 4 Raman spectra of (a) as synthesized and (b) annealed MnO_{4} nanoparticles.

FTIR spectra for as synthesized and annealed nanoparticles are shown in figure 5(a&b). In the region 400 to 700 cm⁻¹, the bands observed at 429 cm⁻¹, 458 cm⁻¹, 513 cm⁻¹ and 609 cm⁻¹ corresponds to the Mn-O vibrations ascribed to the stretching modes of octahedral and tetrahedral sites of MnO_{4} [16]. The bands at 1110 cm⁻¹ and 1633 cm⁻¹ are due to the O-H bending vibrations along with Mn [17]. The broad absorption peak at 3443 cm⁻¹ indicates the presence of hydroxide group. Annealed nanoparticles exhibits an extra peak observed at 995 cm⁻¹ which may be attributed to M=O vibration of MnO_{4}.
3.4 Morphological Studies
HRSEM micrographs of as synthesized and annealed nanoparticles are shown in figure 6(a-c & d-f), which shows irregular shaped disk like morphology with average particle size of about 155 nm. Annealed nanoparticles also exhibit similar morphology with average particle size of about 400 nm.

TEM micrograph (figure 7) of as synthesized nanoparticles was also taken as supporting information. It confirms similar morphology with particle size of 155 nm.

3.5 Magnetic studies
Magnetic behaviors of as synthesized and annealed Mn$_3$O$_4$ nanoparticles are shown in figure 8. This magnetic study was carried out in room temperature with maximum magnetic field at 15 KOe. Both as synthesized and annealed Mn$_3$O$_4$ nanoparticles exhibit paramagnetic behavior. The maximum magnetizations observed were 0.2864 emu/g and 0.5347 emu/g for as synthesized and annealed nanoparticles at maximum field. Magnetic ordering of annealed samples is increased with increase in crystallinity of the samples. [19]

4. CONCLUSION
Mn$_3$O$_4$ nanoparticles were synthesized by co-precipitation method and their annealing effect was reported. PXRD revealed mixed phases of Mn$_3$O$_4$ and Mn$_2$O$_3$. Annealing of nanoparticles at 300 °C has favored the growth orientation towards Mn$_2$O$_3$ phase due to oxidation of Mn$_3$O$_4$. Increased peak intensity and decreased microstrain and dislocation density indicates the increase in crystallinity for annealed samples. XPS spectra proved the presence of Mn and O with presence of no other impurities. EDS also confirmed the composition of the samples. HRSEM micrographs showed irregular shaped plates with average particle size of 155 nm for as synthesized particles and 400 nm for annealed particles. TEM micrograph further confirmed similar morphology with particle size almost same as 155 nm. Functional studies were carried out using micro Raman and FTIR. Various bending and stretching modes of Mn-O and O-H groups were analyzed from these spectroscopic studies. Room temperature magnetic studies confirmed that the paramagnetic behavior of Mn$_3$O$_4$ nanoparticles improved for annealed samples due to increase in crystallinity.
5. REFERENCES


