Investigation of the effect of annealing temperature on photophysical properties of manganese dioxide nanostructure prepared via co-precipitation route

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Abstract. Co-precipitation method was used to synthesize Manganese dioxide (MnO₂) nanostructures. The synthetization of Manganese dioxide (MnO₂) requires Manganese dichloride tetrahydrate (MnCl₂·4H₂O), Sodium hydroxide (NaOH) and distilled water. Manganese dioxide nanostructures were synthesized by taking suitable amount of manganese dichloride tetrahydrate and mixing it with 100 mL of distilled water. Sodium hydroxide (NaOH) was added to the precursor solution to adjust pH 12 and stirred for 18 hours. The prepared MnO₂ nanoparticles were characterized through various techniques such as X-ray diffraction (XRD), UV-visible spectroscopy and scanning electron microscopy (SEM). XRD results revealed that MnO₂ had tetragonal single phase. Average crystallite size for prepared samples is found in the range 39 to 45 nm. It is increased with increasing of annealing temperature. Volume and density of unit cell are found to be 258.83 Å³ and 4.522 g/cm³ respectively. SEM results showed that the annealing temperature has affected the shape of MnO₂. The morphology of MnO₂ changed from spherical to rod-like shape as annealing temperature increase. Absorption peaks are obtained between 362 nm to 366 nm of wavelength. These Manganese dioxide (MnO₂) nanoparticles can be applied as catalysts, permeable of toxic metals, ion/molecular-sieves, component of dry cell, inorganic pigment, electrodes for electrochemical batteries, electrodes for supercapacitors and cleaning of water.

1. Introduction
In recent years, research and development is mostly being done on nanotechnology that has delivered nanostructures (particles with size ≈ 100 nm or less) having physical properties that differ from those of the bulk counterparts and depend on polymorphism, morphology, size of particles, size distribution, coating, and the precursor used in the synthesis [1]. With the need for renewable energies, these nanomaterials have undergone extensive research, to develop new systems that can be used for energy storage and conversion. Among them, transition-metal oxides including TiO₂, MnO₂, V₂O₅, etc. are stable and robust materials with tunable properties offering large surface areas.

Over the last three decades nanoparticles have received an increasing amount of research interest [2] Nanoscale materials have proved to have unique properties than its bulk due to large surface to volume ratio. MnO₂ nanoparticles are one of the most attractive oxides due to their unique properties as a low band gap, high optical constant semiconductor that exhibits ferroelectric and catalytic properties. MnO₂ is natural abundant, cheaper, and low toxic nanomaterials. In Ancient times, mineral-MnO₂ (MDOs) are utilized as blackish pigment for painting the rocks in Paleolithic pothole of the
Magdalenian traditions [3]. As a kind of important metal oxide, manganese dioxide is one of the most attractive inorganic materials because of its physical and chemical properties and wide applications in catalysis [4] molecular-sieves [5] ion exchange, biosensor, and especially energy storage.

Electrical properties of MnO$_2$ Nano-material basic research are the key to the development of future applications in electronics. MnO$_2$ has a considerable gap of approximately 1.3 eV at room temperature. MnO$_2$ exhibits specific capacitance within the range of 50-200 F/g in aqueous electrolyte, lesser than its $C_{\text{theoretical}}$ 1370 F/g [6]. MnO$_2$ based supercapacitors are ultimately restricted by poor electrical conductivity of MnO$_2$. The incorporation of other metal elements with MnO$_2$ improve their electrical conductivity and charge storage capacity. This can be achieved by mixing supplementary transition metal oxides such as RuO$_2$, NiO, Co$_3$O$_4$ with MnO$_2$ to make assorted metal oxides [7].

Manganese oxides with channel and layered crystal structures constitute a large family of porous materials. Manganese oxide (MnO$_2$) has a number of polymorph structures. The manganese dioxide found in different crystalline structures, including $\alpha$-, $\beta$-, $\gamma$-, $\nu$-, $\eta$-, $\delta$-, $\lambda$-MnO$_2$, etc [8]. The MnO$_6$ structural unit is connected in diverse ways. MDOs are non-stoichiometric compounds, because of inevitable structural water molecules that are physisorbed. MDOs crystallize with various morphologies and crystallographic forms [9] including the $\alpha$-, $\beta$-, $\gamma$-, $\delta$-, $\nu$-, $\eta$- and R-polymorphs [10] which are naturally occurring minerals such as hollandite (2×2), pyrolusite (1×1), nsutite (1×1)/(1×2), birnessite (1×∞), akhtenkite (dense stack), spinel (1×1), and ramsdellite (1×2), respectively, where $(m \times n)$ denotes the tunnel dimension [11].

In this research work, Manganese oxides (MnO$_2$) nanostructures were prepared by using co-precipitation technique and effect of annealing temperature on their different properties such as structural, morphological and optical properties were investigated.

2. Experimental setup

2.1. Chemicals and synthesis
All chemicals used throughout the research were of analytical regent grade and purchased from sigma-Aldrich. For the preparation of Manganese Dioxide nanoparticles schematic diagram is shown in figure 1. The Manganese Dioxide nanoparticles were synthesized by precipitation method using Manganese dichloride tetrahydrate [MnCl$_2$.4H$_2$O] and sodium hydroxide (NaOH) as precursors the MnCl$_2$.4H$_2$O and NaOH in distilled water [12]. The obtained solution was stirred continuously using the magnetic stirrer for 8 hours.

![Figure 1. Schematic diagram of MnO$_2$ synthesis.](image-url)

Sodium hydroxide solution (5 M) was added drop by drop to the MnCl$_2$.4H$_2$O solution. The reaction could proceed for complete addition of sodium hydroxide solution, pH was maintained at 12.
The solution was kept overnight for aging. The solution was filtered and washed three times with distilled water to remove the by-products. The moisture free content was obtained after drying at 80 °C for 5 hours in an oven (Model: Shel-Lab). Then the grinded samples were annealed at different temperatures of 500 °C, 600 °C, and 700 °C in furnace (Model: SNOL-LHM01).

2.2. Characterization
The powder X-ray diffraction (XRD) was performed through XRD system Model (PANalytical) with Nickel filtered CuKα (λ=1.50405) radiation [13]. The particle size was calculated from broadening of line by using Scherrer’s formula. The scanning electron microscope (SEM) studies were performed by using SEM Model (JEOL- JSM 5910) to study the morphology of the prepared nanoparticles.

3. Results and discussion

3.1. Structural analysis
The XRD pattern of NnO₂ nanoparticles prepared at 500 °C, 600 °C, 700 °C and untreated is shown in figure 2. The shown XRD pattern confirms the formation of nanoparticles. The MnO₂ nanoparticles are observed to be highly crystalline. Peaks at 2θ of 18.01°, 28.94°, 38.18°, 49.39°, 55.19°, 59.92°, 65.85° were referred to XRD planes (200), (310), (211), (411), (600), (521), (002). The XRD results showed that Manganese dioxide has the tetragonal structure. The average crystallite size of prepared MnO₂ nanoparticles is calculated by using Scherrer’s relation as shown by equation (1).

\[ L = \frac{0.9 \lambda}{\beta \cos \theta} \]  

(1)

where \( L \) is the crystal size, \( \beta \) is the line width (FWHM), \( \theta \) is the diffraction angle and the \( \lambda \) is the wavelength of X-ray radiation.

The lattice parameters, volume of unit cell and density of unit cell are presented in table 1. The values of lattice parameters for all the samples were calculated by using equation (2). The lattice parameter was not considerably influenced by the annealing temperature. These parameters are matching with the reported values of PDF file No. 44-0141.

\[ \frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \]  

(2)

The volume of unit cell was calculated by using equation (3) by using the lattice parameter values from table 2. There is no significant effect of annealing temperature on the volume of unit cell.

\[ V_{cell} = a^2c \]  

(3)

The X-ray density was calculated by using equation (4).

\[ D = \frac{Z M}{N_A V_{cell}} \]  

(4)

Where \( Z \) is the number of molecules per unit cell, \( M \) is the molar mass of the Zinc Oxide, \( N_A \) is Avogadro number, \( V_{cell} \) is the volume of the unit cell.

Table 1. Structural parameters extracted from XRD data of samples.

| Sample | Lattice constant a=b (Å) | Lattice constant C (Å) | Unit cell Volume (Å³) | Unit cell Density g/cm³ | Particle Size (nm) |
|--------|--------------------------|------------------------|----------------------|-------------------------|------------------|
| A      | 9.98                     | 2.687                  | 267.62               | 4.3150                  | 39.10            |
| B      | 10.01                    | 2.837                  | 284.22               | 4.0630                  | 29.25            |
| C      | 9.9804                   | 2.117                  | 210.84               | 5.4772                  | 39.75            |
| D      | 9.836                    | 2.818                  | 272.671              | 4.2352                  | 45.55            |
Figure 2. XRD pattern of samples A, B, C and D.
Average particles size is increased with increase in temperature treated as shown in table 1. This is because of change in growth rate between the different crystallographic planes.

3.2. SEM analysis
The scanning electron microscope images of prepared manganese dioxide nanoparticles of Sample A, Sample C and Sample D are shown in figure 3. The SEM images show the size and the morphology of the prepared nanoparticles. The SEM images show that the particles have random size and their morphology was changed from spherical to rod-like shape with increasing temperature.

![SEM images](image)

**Figure 3.** SEM micrographs for (a) Samples A, (b) Sample C and (c) Sample D.

3.3. UV visible analysis
Absorption spectra of prepared samples are obtained by UV Visible spectrometer. For UV-Vis studies a small amount of MnO₂ (0.02 g) for all samples is dissolved in 20 mL distilled water and stirred in sonicator. Graphs for absorption data for samples A, B, C and D are shown in figure 4.
Optical properties of Manganese Dioxide Nanoparticles were analyzed using UV-Visible spectra. Absorption peak was observed at different wavelengths for all samples. Peaks were observed between 362 nm to 366 nm for all samples.

4. Conclusion
Manganese Dioxide nanoparticles samples are prepared by coprecipitation method. All samples are treated at different temperatures, i.e, 500 °C, 600 °C, 700 °C and a sample was kept untreated. Structured, morphological, and optical properties were characterized by XRD, SEM and UV visible. It is concluded that heat treatment on prepared samples of Manganese dioxide nanoparticle has affluence on particle size, volume and density of unit cell. Tetragonal structure and random particle size of MnO₂ was noted. Absorption peaks for prepared samples was observed between 362 nm to 366 nm. With increase in temperature particles agglomerated and rod-like shape is formed.

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