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Synthesis, Characterization and Study of Antimicrobial Activity of Amino Functionalized Manganese Oxide Nanoparticles

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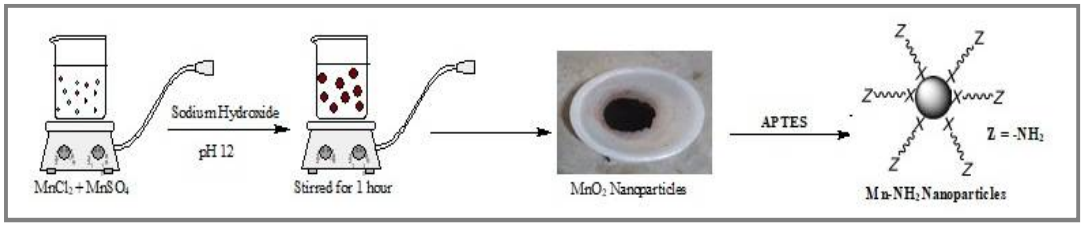
ABSTRACT

Manganese oxide nanoparticles find significant applications in advanced materials like batteries, water treatment and imaging contrast agents. In this work manganese oxide nanoparticle with controlled particle size was synthesized by co-precipitation technique under a fine control of pH using NaOH solution. The MnO_2 nanoparticles thus synthesized were treated with 3-aminopropyl triethoxysilane (APTES) and amino functionalized manganese oxide (MnO_2-NH_2) nanoparticles were obtained. The optical properties of nanoparticles were analyzed using UV-Vis spectrophotometer. The characteristic functional group present was analyzed using FTIR spectrophotometer. The surface morphology and particle size were studied by SEM and XRD analysis. TGA study was carried out to check the thermal stability of the manganese oxide nanoparticles. Antimicrobial activity of MnO_2 and MnO_2-NH_2 towards the both gram negative bacteria (Escherichia coli) and gram positive bacteria (Staphylococcus aureus) was studied using serial dilution method.

Graphical Abstract



Keywords: MnO_2 nanoparticles, MnO_2-NH_2nanoparticles, Surface functionalization.

INTRODUCTION

Nanostructured materials have been comprehensively explored for the fundamental scientific and technological interests in retrieving new classes of functional materials with exceptional properties and applications [1]. In current years, there has been a growing interest in the synthesis of nanosized crystalline metal oxides because of their large surface areas, unusual adsorptive properties, surface defects and fast diffusivities. In technological applications, oxides are used in the building of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts [2]. Oxide nanoparticles can exhibit distinctive physical

and chemical properties due to their limited size and a high density of corner or edge surface sites. Hence transition metal oxides are the most widely used in the emerging field of magneto-electronics, catalysts, and photo catalysis, solar-cells, and gas- sensors applications [**3**].

Manganese dioxide nanoparticles are of ample importance in technological applications and have been intensively inspected as promising electrode material in primary/secondary batteries and electrochemical capacitors due to their admirable electrochemical properties, low cost, environmentally benign and ease of preparation. Physical vapour deposition, Chemical vapour deposition, Electrodeposition, Sol-gel process, aerosol processing, mechanical alloying/milling are some of the commonly used methods by which nanoparticles can be synthesized. The Co-precipitation method is commonly employed because it is cost effective and has so many advantages [**4**]. Nanostructure manganese dioxide has been considered as an idyllic electrode material for energy storage, such as super capacitors (also known as electrochemical capacitors) [**5, 6**]. MnO_2 nanoparticles are employed in water treatment and imaging contrast agents [**7**]. MnO_2 is considered as one of the best catalysts due to its low cost, less toxicity and environmental compatibility. Among many transition metal oxides, manganese oxide exhibit different forms 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 [**5**].

Properties of nanoparticles are different to those of matter of the same chemical composition on a larger scale. Therefore, research on nanoparticles is increasing hastily, and copious applications are anticipated. Though some nanomaterials have brilliant physical and chemical bulk properties, they do not own apt surface properties for specific applications. Surface atoms make a large contribution to the thermodynamic characteristics of solids, particularly in the case of nanoparticles where such atoms determine structural transitions. The specific heats of phase transition, and other fundamental physical characteristics are drastically changed when the particles are of nano scale size. It is also worth noting that these and other physical characteristics such as melting point of crystallites, the pressure needed for crystalline structure rearrangement, ionization potentials, bond energies and intra-atomic distances, optical and magnetic properties, etc. are essentially changed in non-monotonic ways as the particle size continues to decrease within the nanoscale range [**8**]. Thus, it may be necessary to amend the surface of such materials.The most common way to do so is to attach suitable organic groups to the surface atoms. Surface modification can stabilize nanoparticles against agglomeration and render them compatibility with another phase. In this work the MnO_2 nanoparticles are surface functionalized with 3-aminopropyltriethoxysilane. The surface functionalized MnO_2 nanoparticles were relatively less agglomerated. The surface functionalization enables self-organization [**9**]

Metal oxide nanoparticles are the most hopeful as they show commendable antimicrobial properties due to their large surface area to volume ratio which increasing the microbial resistance to metal ions and its non-toxic nature when compared to organic disinfectants [**10**]. Hence, metal oxide nanoparticles have been engrossed by researchers to use in biomedical and pharmaceutical applications as alternative effective microbial inhibitors. The investigation of antimicrobial activity of MnO_2 and MnO_2-NH_2 was made against gram negative bacteria *E.coli* and gram positive bacteria *S. aureus* through serial dilution method. In this work we have reported the synthesis of MnO_2 nanoparticles using co-precipitation technique and its surface modification using APTES. We have also reported the structural, optical and thermal properties. Additionally we have performed the antimicrobial activity of MnO_2 and MnO_2-NH_2 nanoparticles.

MATERIALS AND METHODS

Manganese chloride and Manganese sulphate, Sodium hydroxide, Ethanol, (3-Aminopropyl) triethoxysilane (APTES), and other chemicals used in the study were of analytical grade and were purchased from Merck and Aldrich.

Characterization tools: The characterization of nanoparticles were determined by the aid of UV-Visible spectroscopy (Systronic-2203) in the wavelength range 200-1000 cm^{-1}, Infra-red Spectroscopy (SHIMADZU 8300), SEM (ZIESS ULTRA 55) and XRD using (RIKAGU using CuKα1, λ=0.15406 nm radiations). Thermogravimetric analysis (SDT Q600 V20.9 Build 20)

Synthesis of Manganese oxide Nanoparticles: The co-precipitation method was performed by using manganese salts of two different anions which are manganese (II) sulphate and manganese chloride. Both salts of equal concentration i.e., 0.2M are mixed with continuous stirring at a constant temperature of 60°C. While stirring, NaOH solution was added till the pH of the solutions become 12. The stirring was continued for 1 h at constant temperature of 60°C. Brown precipitates formed was then filtered and washed with ethanol. Precipitates were dried for overnight at 100°C. Then the precipitate was kept in muffle furnace at 500°C for 4 h.

Synthesis of amino functionalized MnO_2 nanoparticles: APTES functionalized MnO_2 nanoparticles were prepared by re-dispersing the MnO_2 nanoparticles (0.2 g) in 25 mL of ethanol containing certain volume of APTES. The solution pH was adjusted to 5.0 using acetic acid. A sonication treatment was followed at 40ºC for 2 h. After that, the solid was centrifuged, washed with ethanol and dried under vacuum at 60ºC for 24 h. The obtained samples were labelled as APTES-MnO-x, and the x value indicated the addition volume (mL) of APTES.

RESULTS AND DISCUSSION

X-Ray Diffraction (XRD) analysis was carried out on powder form and typical diffraction patterns are shown below. From these graphs we can find the size of the crystallites by using Debye-Scherer equation as illustrated below:

$$\mathbf{D = K \lambda / \beta \cos\theta}$$

Where, D is the average crystallite size, K is a constant depend on the crystallite shape (0.94), is the X-ray wavelength (in this case, 1.54Å for Cu-Kα radiation), β is the full width at half maxima (FWHM), and θ is the Bragg's angle. Using the above equation we can determine the size of the particles.

Figure 1 shows X-ray diffraction study of manganese oxide metal nanoparticles synthesized by co-precipitation method. From the XRD pattern it is clear that manganese oxide metal nanoparticles synthesized were purely crystalline in nature. The peak at 2θ = 36°00', indicates the formation of tetragonal MnO_2. The peak was indexed to (2 1 1) planes which is in good agreement with the JCPDS (044-0141) values [**11**]. Average particle size of manganese oxide nanoparticles was found to be 25.0 to 30.0 nm. Size of MnO_2 nanoparticles corresponding to 100% intensity peak correspond to 25.93 nm as calculated using Scherrer equation.

Figure 2 shows the X- ray diffraction pattern of amino functionalized MnO_2 nanoparticles. It is clear that the amino functionalized manganese oxide nanoparticles were also crystalline in nature. Size of MnO_2-NH_2 nanoparticles corresponding to 100% intensity peak were 27.99 nm. The increase in the size of the nanoparticles may be attributed to the surface functionalization with amino. The peaks at 2θ = 35º84′ confirmed the presence of manganese.

SEM analysis is carried out to study the surface morphology of the nanoparticles. In the present work MnO_2 nanoparticles were synthesized by the co-precipitation technique. SEM image of manganese oxide nanoparticles is shown in the figure 3. Manganese oxide nanoparticles with the mean diameter of 27 nm were synthesized using manganese chloride and manganese sulphate as the metal

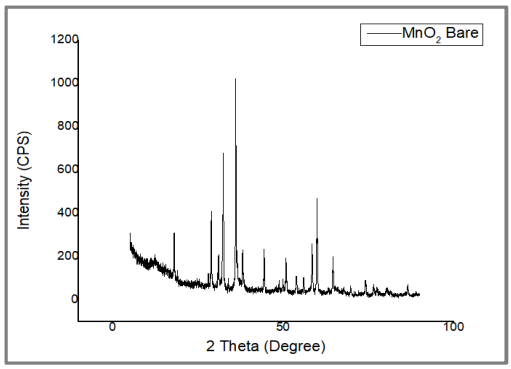


Figure 1. XRD Pattern of MnO_2 Nanoparticles

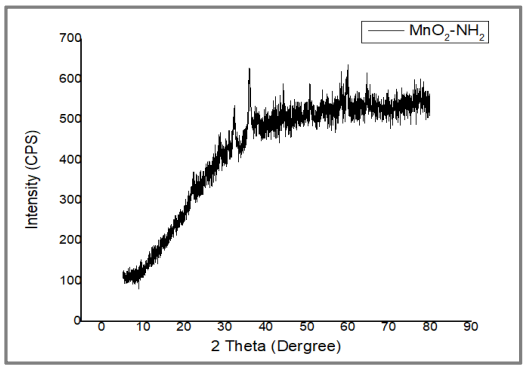


Figure 2. XRD Pattern of MnO_2-NH_2 Nanoparticles

source and NaOH as the precipitating agent. The SEM image reveals that the nanoparticles synthesized were spherical in nature. The elemental analysis of manganese oxide nanoparticles was carried out by Energy Dispersive Spectrum on the SEM. Figure 4 shows the EDS spectrum of spherical nanoparticles prepared. The peaks around 0.5 keV and 6.0 keV correspond to the binding energy of oxygen and manganese respectively. The rest of the lines in the EDS spectrum correspond to other elements (Na).

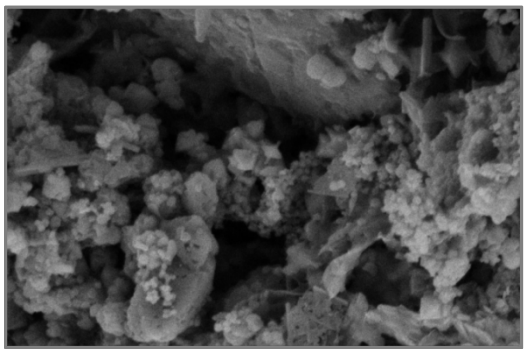


Figure 3. SEM Image of MnO_2 Nanoparticles

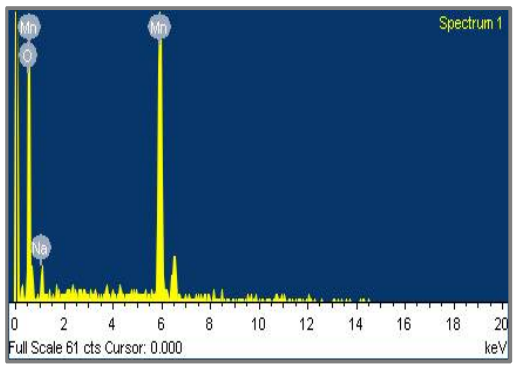


Figure 4. EDS Image of MnO_2 Nanoparticles

The IR spectrum of amino functionalized silica nanoparticles is given below (Figure 5). Oxides and hydroxides of metal nanoparticles generally gives absorption peak in the finger print region i.e. below wavelength of 1000 nm arising from inter-atomic vibrations. The bands at 520 cm^{-1} and 613 cm^{-1} correspond to the Mn–O bond [**12-14**].The bands at 3444.98 cm^{-1} and 3425.69 cm^{-1} correspond to the absorption frequency of $–NH_2$ group. The small band at 3402.54 cm^{-1} corresponds to the O-H stretching. The peak at 2922.25 cm^{-3} indicates the $–CH_3$ stretching. The absorption peak at 1381.08 cm^{-1} may be due to $–CH_2$ stretching. From the above result we conclude that the manganese oxide nanoparticles were surface functionalized with $–NH_2$ group.

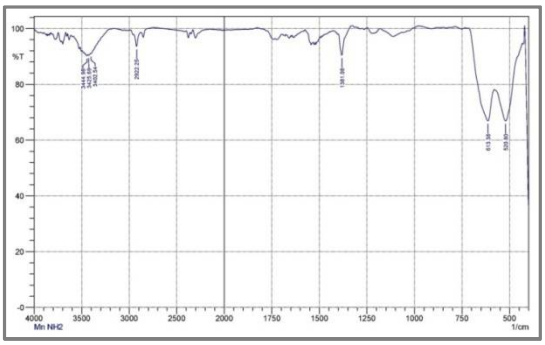


Figure 5. IR Spectrum of MnO_2-NH_2.

Figure 6 shows UV-Visible spectra of manganese oxide metal nanoparticles synthesized by co-precipitation method as a function of wavelength. The UV-Vis spectral data of the nanoparticles were measured using distilled water as the reference sample in the wavelength range from 200-800 nm. The UV-Visible absorption shows sharp absorption at 339.60 nm due to manganese oxide metal nanoparticles. The characteristic absorption at 339.60 nm is attributed to the ligand to d-d transitions.

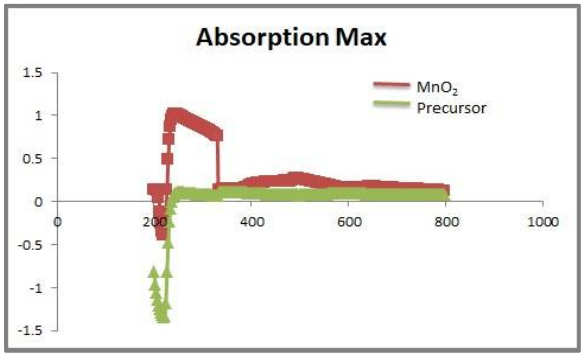


Figure 6. UV-VIS Spectrum of MnO_2 Nanoparticles.

The simultaneous analysis of TGA/DSC analysis of manganese oxide nanoparticles was studied where the heating rates were suitably controlled at 10ºC per minute under nitrogen atmosphere and the weight loss was studied from ambient temperature to 1000ºC. The TGA/DSC representative thermogram is given in figure 7. The decomposition curve indicates that in the first decomposition stage up to 100°C (7.34%), the molecules of water adsorbed from moisture are lost. In the second stage thermal decomposition of MnO_2 to Mn_2O_3 takes place in the temperature range of 150ºC to 300ºC (7.02%). The weight loss in the temperature range of 625ºC to 650ºC (6.74%) corresponds to the decomposition of Mn_2O_3 to Mn_3O_4. The residual weight (78.88%) indicates that the MnO_2 nanoparticles are thermally stable [**15**]. The DTA curve indicates that the decomposition of manganese oxide nanoparticles is an exothermic process. The peak at 650ºC is attributed to the melting point of manganese oxide nanoparticles. DSC studies reveal that the glass transition temperature is 250ºC.

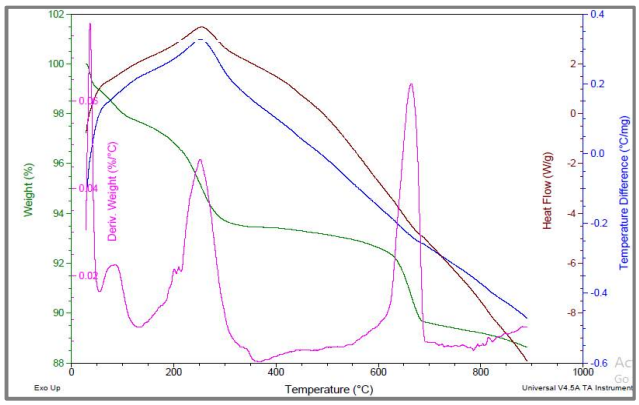


Figure 7. TGA/DSC Curves of MnO_2 Nanoparticles.

The newly synthesized compounds were screened for their anti-microbial activity against gram-positive and gram-negative bacteria. It was performed by serial dilution method. The result of the anti-microbial activity is as shown in table below both MnO_2 and MnO_2-NH_2, showed positive result against gram-positive and gram-negative bacteria. It is clear from the data given that the functionalized nanoparticles showed more inhibition than the bare metal oxide nanoparticles. So the functionalized nanoparticles exhibit better anti-microbial activity. On comparing the results given in table 1 and table 2, we can say that MnO_2 nanoparticles showed greater antimicrobial activity for *S.*

aureus than *E.coli*. In case of *E coli* 10^{-2} µg mL^{-1}, 10^{-3} µg mL^{-1} served to be the minimum inhibitory concentration (MIC) for MnO_2 and MnO_2-NH_2 respectively while in case of *S aureus* 10^{-2} µg mL^{-1}, 10^{-3} µg mL^{-1} served as the MIC for MnO_2 and Mn-NH_2 respectively (Figure 8 and 9).

Table 1. Antimicrobial activity of nanoparticles against *E. coli*

Nanoparticles	*Escherichia coli* (Gram negative)				
	10^{-5} µg mL^{-1}	10^{-4} µg mL^{-1}	10^{-3} µg mL^{-1}	10^{-2} µg mL^{-1}	10^{-1} µg mL^{-1}
MnO_2	+	+	+	-	-
Mn-NH_2	+	+	-	-	-

Table 2. Antimicrobial activity of nanoparticles against *S.aureus*

Nanoparticles	*Staphylococcus aureus* (Gram positive)				
	10^{-5} µg mL^{-1}	10^{-4} µg mL^{-1}	10^{-3} µg mL^{-1}	10^{-2} µg mL^{-1}	10^{-1} µg mL^{-1}
MnO_2	+	+	+	-	-
Mn-NH_2	+	+	-	-	-

Figure 8a. Antimicrobial activity of MnO_2 nanoparticles for *E.coli*

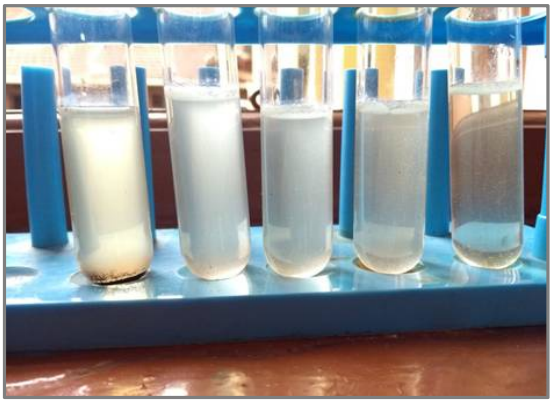


Figure 8b. Antimicrobial activity of MnO_2-NH_2 nanoparticles for *E.coli*

Figure 9a Antimicrobial activity of MnO_2 nanoparticles for *S.aureus*

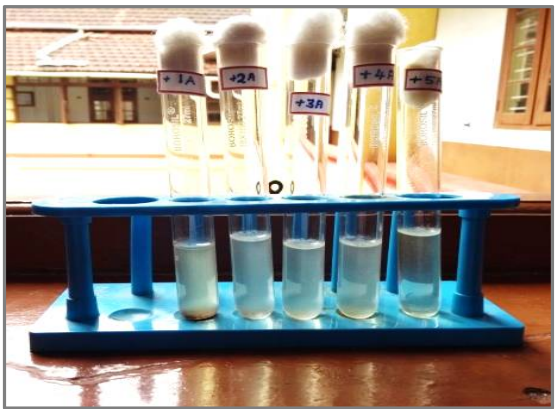


Figure 9b. Antimicrobial activity of MnO_2-NH_2 nanoparticles for *S.aureus*

APPLICATION

MnO_2 metal nanoparticles have vast applications, in the field of electrode materials, Biosensors, nanowires, nanofibres and as antimicrobial agent.

CONCLUSION

- Manganese oxide nanoparticles were successfully synthesized using Co-precipitation method and were surface functionalized with functional group. The SEM analysis revealed that the manganese oxide nanoparticles synthesized had a spherical morphology.
- The EDS analysis carried out on the SEM image confirmed the presence of manganese in the nanoparticles.
- The XRD studies showed that the MnO_2 and MnO_2-NH_2 were all crystalline in nature and had the particle size of 25.00nm and27.99nm respectively as calculated from the Scherrer equation. The MnO_2 nanoparticles have tetragonal structure; the 2θ and FWHM values were in good rapport with the standard JCPDS values.
- The UV-VIS spectrum shows a sharp absorption peak at 339.60nm due to the MnO_2 nanoparticles.
- The IR spectrum of MnO_2-NH_2 shows the characteristic Mn-O stretching bands along with the characteristic peaks for the presence of $–NH_2$ functional group.
- The thermal analysis of MnO_2 shows that the compound is thermally stable.
- The MnO_2 and MnO_2-NH_2 showed excellent antimicrobial activity.

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