

Synthesis and Structural Properties of Doped and Un-doped MnO₂ Nanoparticles for its Use in Percussion Instruments

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Abstract

The thrust to develop eco-friendly procedures for the production of nanoparticles arises from the adverse environmental conditions. Keeping the possible consequences in mind manganese dioxide (MnO₂) and Ag doped MnO₂ nanoparticles were synthesized by co-precipitation method. Manganese dioxide nanostructures are of considerable importance in technological applications due to their excellent electrochemical properties, low cost, environment friendly nature and ease of preparation. Co-precipitation method is an easy method of synthesis of nanoparticles. This method can produce fine, stoichiometry particles of single and multicomponent metal oxides.

The structural characterization was carried out using Powder X-ray Diffraction (XRD) method and Scanning Electron Microscopy (SEM). SEM images showed that the particles are irregular in shape with varying sizes. Energy Dispersive X-ray Spectroscopy (EDAX) analysis confirms the presence of manganese, oxygen and iron. The size of MnO₂ and Ag doped MnO₂ nanoparticles was calculated using x-ray diffraction method. The average particle size of MnO₂ nanoparticles was 12 nm and for Ag doped nanoparticles was 8 nm.

Keywords

Ag doped MnO₂ nanoparticles, co-precipitation method, x-ray diffraction, SEM, EDAX

I. INTRODUCTION

Nanotechnology means the creation and use or manipulation of matter on the atomic scale. By prefiguring matter on the nanometer length scale, it is possible to vary physical properties of materials such as stress, strain and adhesion without changing the chemical composition [1-3]. This is due to unique size dependent properties of nanoparticles, which are often thought as a separate and intermediate state of matter lying between individual atoms and bulk material. Using flame test for chemical analysis it was observed that MnO₂ was one of the components of the ink used in percussion instruments.

Some of the commonly used methods for synthesis of nanoparticles are physical vapour deposition, chemical vapour deposition, electro-deposition, sol-gel process, aerosol processing and mechanical alloying/milling. The Co-precipitation method is commonly employed because it is cost effective, less toxic, simple, rapid preparative method, easy control of particle size and less hazardous to environment [4]. Also this method is simple, rapid

preparative method and has easy control of particle size and composition. Co-precipitation of MnO_2 under a fine control of pH by using NaOH solution yields rutile crystal structure.

In the present study, MnO_2 nanoparticles were synthesized using co-precipitation method. As an important functional metal oxide, manganese oxide nanoparticles are one of the most attractive inorganic materials because of its physical and chemical properties. [5, 6]. Present work reports synthesis of MnO_2 nanoparticles and its characterization by XRD techniques and SEM with EDAX.

II. EXPERIMENTAL

MnO_2 and Ag doped MnO_2 nanoparticles were synthesized using Co-precipitation method. All chemicals used in the experiment were of AR grade. The co-precipitation method was performed by using manganese salts of two different anions which are manganese (II) sulphate and manganese oxalate and silver nitrate (AgNO_3).

Both salts of 0.2M concentration are mixed with distilled water and continuously stirred at 600-800 RPM. While stirring, NaOH solution was added till the pH of the solutions becomes 12. The stirring was continued for 2 hours at constant temperature of 60°C . Brown precipitate was formed which was then filtered and washed with ethanol. The precipitate was then dried overnight at 100°C and was kept in muffle furnace at 500°C for 4 hrs to give MnO_2 nanoparticles.

After this MnO_2 nanoparticles were added to ink which is applied on Indian percussion instruments. From previous studies it was known that manganese is one of the major component of ink [7]. With reference to this, doped and undoped MnO_2 nanoparticle were synthesized by co-precipitation method. By changing the proportion of doped and undoped MnO_2 nanoparticles in ink, the effect on particle size of ink was studied.

Likewise, four samples were prepared as indicated below-

1. M1-10 gm ink+1gm of MnO_2
2. M2-10 gm ink+2gm of MnO_2
3. S1 -10 gm ink+1gm of (Ag doped MnO_2)
4. S2 -10 gm ink+2gm of (Ag doped MnO_2)

The structural properties of this sample were studied using a Bruker AXS D8 diffractometer in the range 20° - 80° , with $\text{CuK}\alpha$ radiation. Morphological analysis of the sample was carried out using a JEOL JSM 6360 A scanning electron microscope (SEM).

III. RESULTS AND CONCLUSIONS

A. X-Ray Diffraction

All the samples were characterized by X-ray diffraction (XRD) technique to obtain structural information. XRD pattern of ink is shown Fig.1. XRD patterns of Doped and undoped MnO_2 nanoparticles are shown Fig.2. XRD patterns of ink + MnO_2 nanoparticles are shown in Fig. 3 and XRD patterns of ink + Ag doped MnO_2 nanoparticles are shown in Fig. 4. The well resolved peaks in the XRD patterns clearly indicate polycrystalline nature of the MnO_2 which match well with the characteristic diffraction peaks of MnO_2 (JCPDS card # 44-0141).The observed peaks in all XRD figures for the planes (310), (211), (411), (600), (521), (002) and (541) confirms the phase formation of MnO_2 with pure tetragonal structure [8]. However, it can be noticed that diffraction lines become

broader with Doping of Ag. The crystallite size and lattice structure are known to have their own contributions to the X-ray diffraction peaks, the diffraction peaks in the XRD patterns are strong and sharp, indicating high crystallinity of all the samples.

The X-ray diffraction patterns are studied in detail for the determination of average crystallite size using Scherrer formula [9] as given by equation (1),

$$t = \frac{0.9\lambda}{\beta \cos\theta_b} \quad (1)$$

Where, β is the angular line width at half maximum intensity and θ_b is the Bragg angle for the actual peak.

XRD study reveals that crystallite size of MnO_2 nanoparticles decreases with doping of Ag. It is also observed that when MnO_2 nanoparticles and Ag doped MnO_2 particles are added to Ink, crystallite size decreases.

The x-ray diffraction patterns of the silver doped MnO_2 nanoparticles coincides with the pure MnO_2 nanoparticles and show no diffraction due to addition of silver thus suggesting that silver particles are well dispersed on the MnO_2 surface. Doping with silver does not disturb the crystal structure of MnO_2 indicating that the silver dopants are merely placed on the surface on crystal without being covalently anchored into the crystal lattice. There are no diffraction pattern characteristics of the silver in the XRD patterns. Hence these metal sites are expected to be below the visibility limit of x-ray analysis. The diffraction patterns of pure MnO_2 and Ag Doped MnO_2 samples showed considerable line width, indicating small particles [10]. Table1. indicates that with addition of nanoparticles in ink crystallite size decreases.

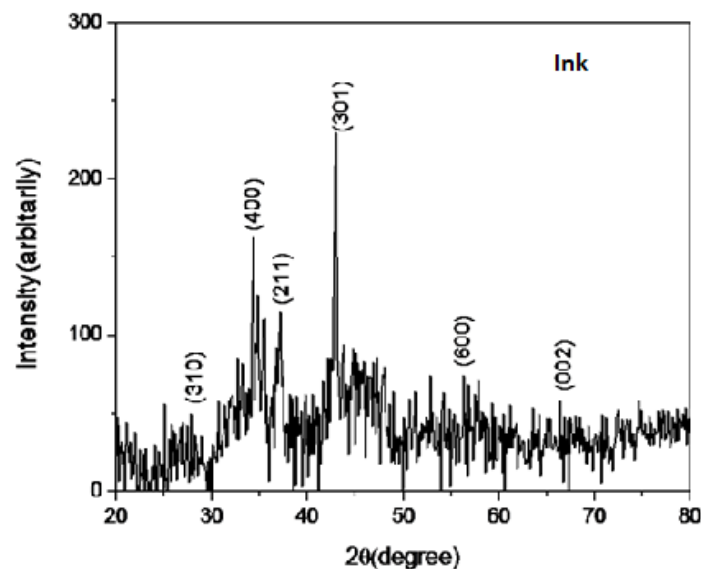


Fig. 1: XRD of Ink

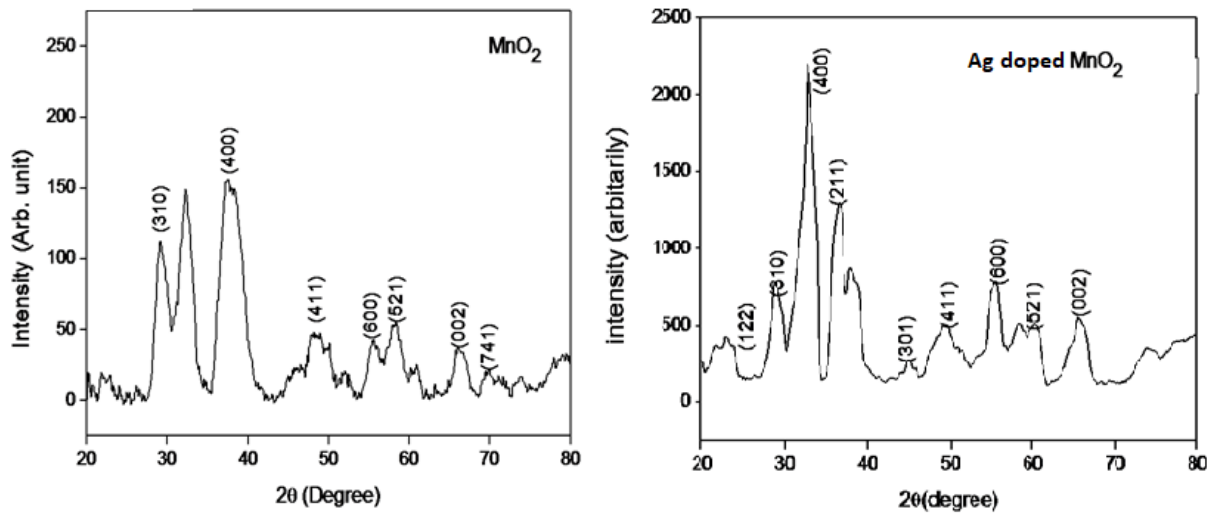


Fig. 2: XRD of Doped and Undoped MnO_2 nanoparticles

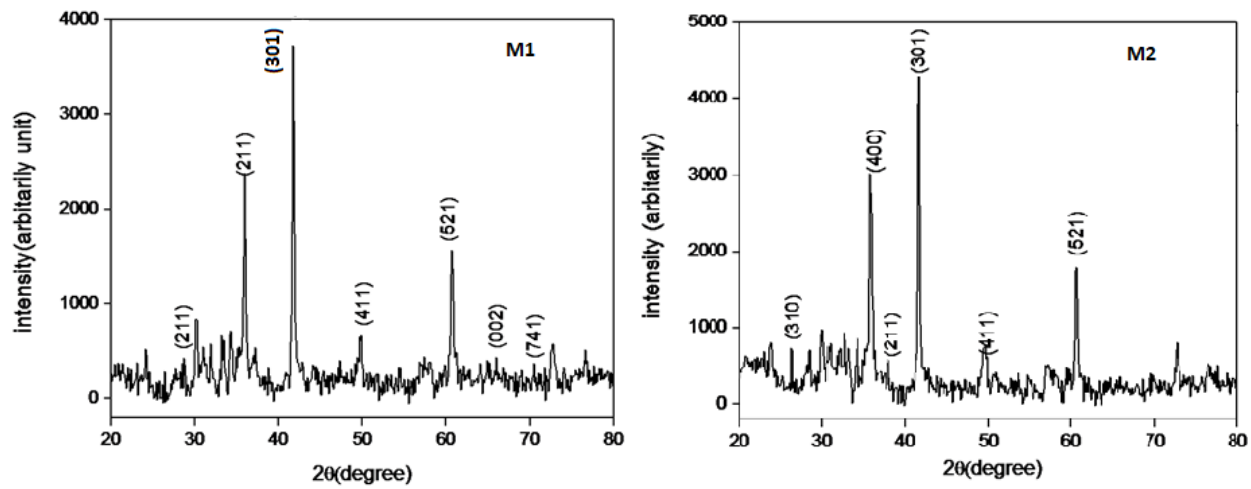


Fig. 3: XRD of ink + MnO_2 nanoparticles

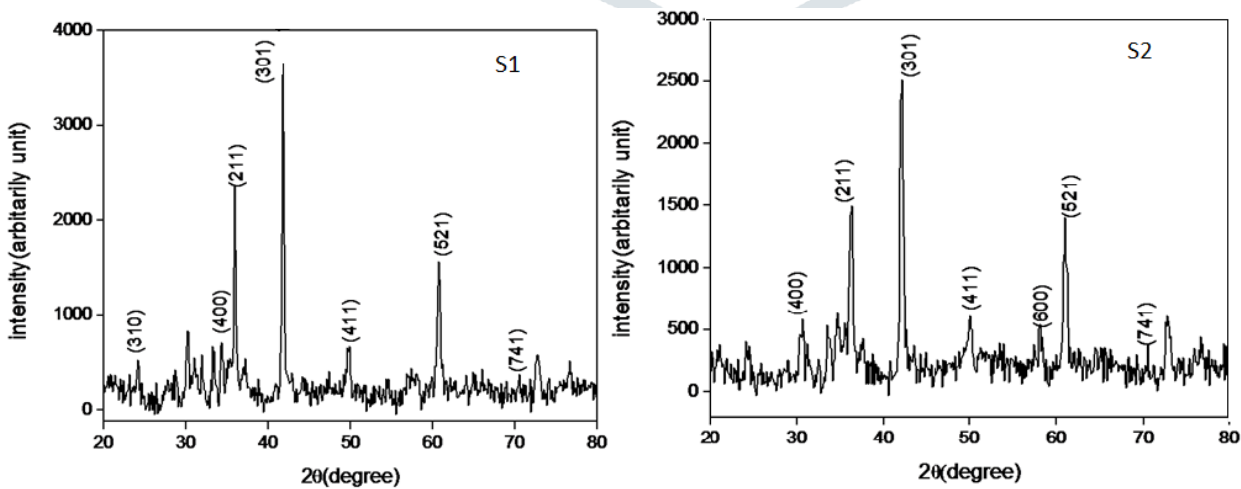


Fig. 4: XRD of ink + Ag Doped MnO_2 nanoparticles

Table 1. Crystallite size from XRD

Sample	Crystallite size from XRD t (nm)
MnO ₂	12
Ag doped MnO ₂	8
Ink	53
M1	48
M2	42
S1	38
S2	32

B. Morphological studies

The surface morphological studies of nanoparticles have been performed by Scanning Electron Microscope (SEM). SEM images and Energy dispersive X-ray analysis (EDAX) spectrum of ink, sample M2 and sample S2 are portrayed in Fig. 5(a), 5(b) and 5(c). It was well documented that the surface morphology has significant impact on performance of nanostructure materials. From SEM images it reveals that ink particles are flake like whereas when MnO₂ and Ag doped MnO₂ nanoparticles are added to ink the particles become spherical in shape. It is also observed that with addition of MnO₂ and Ag doped MnO₂ nanoparticles in ink decreases the size of particles.

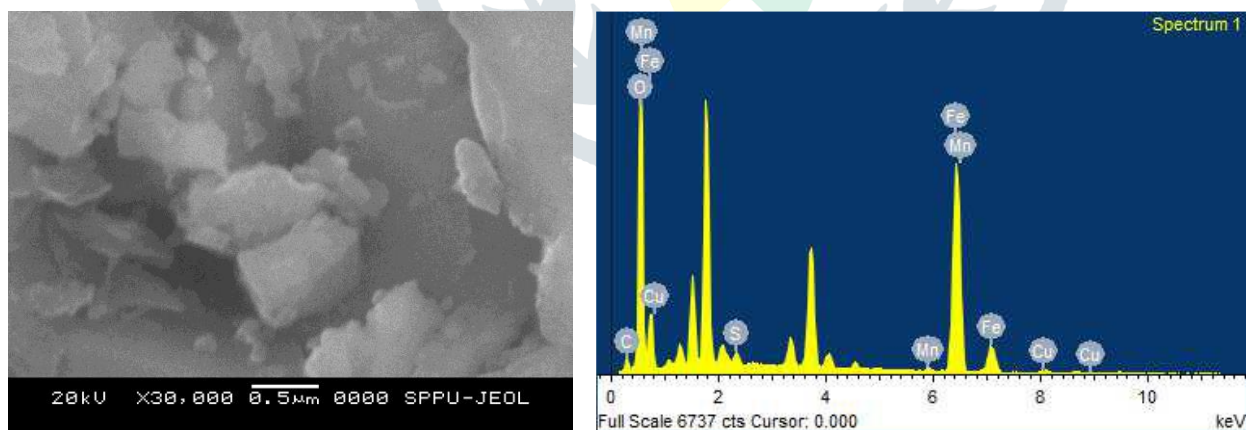
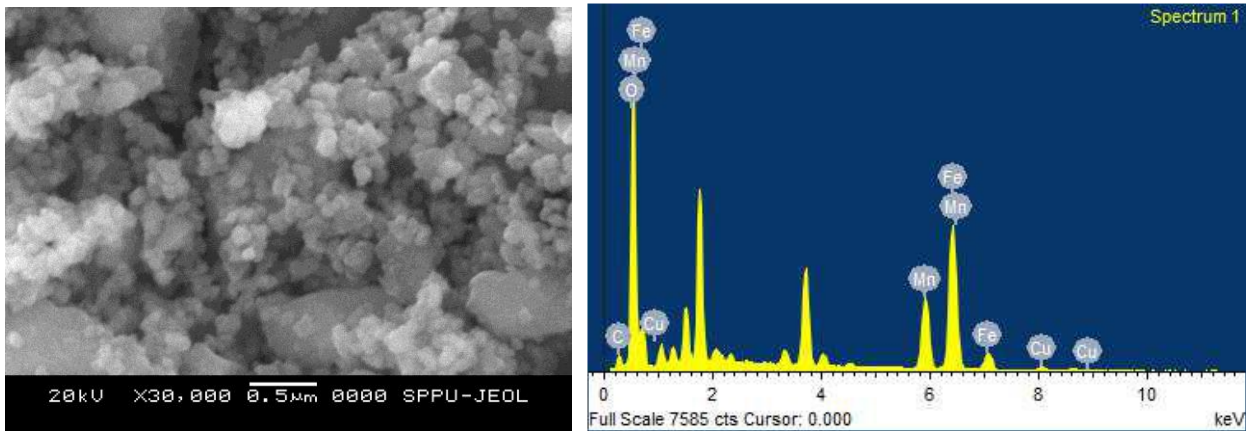
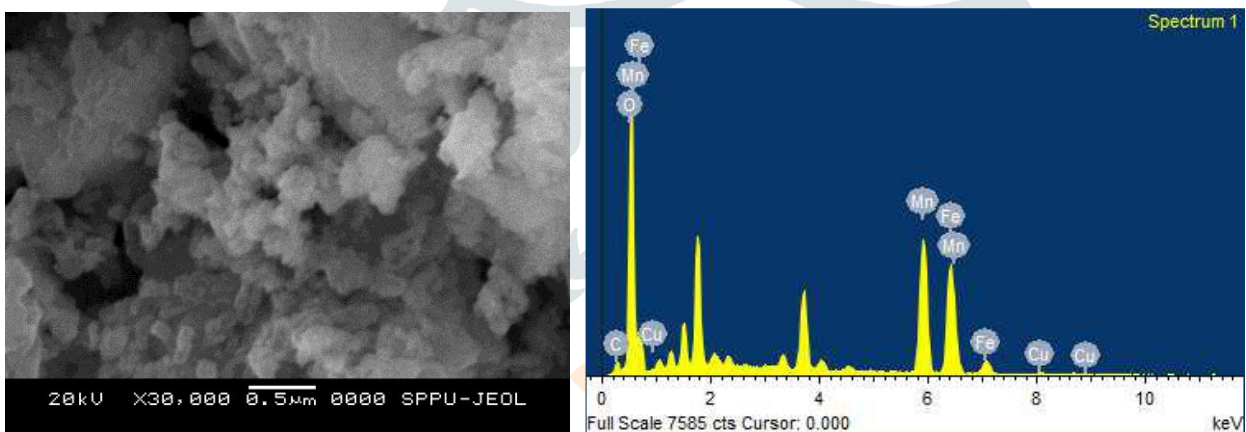


Fig. 5 (a): SEM and EDAX of Ink

Fig. 5 (b): SEM and EDAX of Ink + MnO₂Fig. 5 (c): SEM and EDAX of Ink + Ag doped MnO₂

The Energy dispersive X-ray analysis (EDAX) spectrum of Ink, M1 and S1 samples. The presence of Manganese (Mn), Iron (Fe) and oxygen (O) is confirmed from the EDAX spectrum. Some other elements like sulphur (S), carbon (C) and copper (Cu) are also found in small percentages.

III. CONCLUSION

The characterization and synthesis of MnO₂ and Ag Doped MnO₂ nanoparticles was done by Co-precipitation method. XRD analysis indicates decrease in crystallite size on addition of doped and undoped MnO₂ nanoparticles to the ink. The SEM images reveal that ink particles are flake like whereas when MnO₂ and Ag doped MnO₂ nanoparticles are added to ink the particles become spherical in shape. The EDAX spectrum clearly indicates the presence of Manganese (Mn), Iron (Fe) and oxygen (O) along with some other elements in small percentage. This enhancement in structural and morphological properties of ink with addition of nanoparticles would be helpful in improving tonal quality of percussion instruments in future.

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