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A Study on Synthesis and Assessment of Thermal Stability of MnO_2-Ag Nano Composites

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Abstract

Manganese dioxide (MnO_2) is a versatile material with remarkable physicochemical properties, making it as an essential material. Silver Nanoparticles (Ag-NPs) have significance for their unique property, thermal Stability. In the present research, MnO_2-Ag nanocomposites were synthesized by the hydrothermal method in three different ratios, viz., 1:2(B-1), 1:1(B-2), and 2:1(B-3), respectively. The synthesized nanocomposites were characterized by Thermogravimetric Analysis(TGA) and confirmed by its thermogram that the composite 1:1(B-2) has higher thermal stability(20-600°C range) compared to the thermal stabilities of the remaining composites 1:2(B-1) and 2:1(B-3) respectively. The nanocomposites MnO_2-Ag (B-1) with 1:2 ratio exhibited lower thermal stability and may be considered for use as a suitable component in electric storage batteries like Zinc Air batteries. Other composite B-2(1:1) and B-3(2:1) due to its higher and moderate thermal stabilities, their electrical conductivities increases and it can find use by the end user for suitable application as per the need in a manufacturing industry.

Keywords: Synthesis, Nano Composite, Analysis, Thermal Stability, Thermogram

1. Introduction

Synthesis and Characterization of MnO_2-Ag nanocomposites is one of the areas of research in Nanoscience and Technology. Manganese dioxide (MnO_2) is predominant for its applications in energy storage, environmental remediation, and catalysis. Silver nanoparticles (Ag NPs) are significant for their antibacterial properties, optical behaviour, and catalytic efficiency. In microbiology and materials science, using functionalized nanoparticles has become an important interdisciplinary nature at present. The exploration and creation of advanced synthetic materials rely on refined analytical and design methodologies[1]. Literature review revealed that silver (Ag)-doped manganese dioxide (MnO_2) nanostructures exhibit excellent thermal stability[2]. Research studies also suggested that nanocomposites synthesized through the hydrothermal method under controlled temperature and reaction conditions, would have an impact on their morphology [3]. The MnO_2-Ag composites has acquired substantial interest due to their synergistic benefits. Research studies show that free silver ions are cytotoxic to many human cell lines, but when combined with MnO_2, the ions are stabilized, leading to reduce toxicity [4, 5, and 6]. According to literature reviews, the metal doping can greatly increase the thermal stability and conductivity of MnO_2 nanocomposites. Silver (Ag) doping in MnO_2, in particular can augment its thermal conductivity due to its high thermal and electrical conductivity of silver. The integration of Ag into the MnO_2 matrix can explain the structural modification which can enhance its improved thermal conductivity, and its synergistic effects making it suitable for applications in catalysis, energy storage, and thermal management systems [7, 8, 9, and 10].The combination of silver with MnO_2 materials find their use in thermoelectric devices[11].Ag doping stabilizes the MnO_2 and reduce its weight loss and shifts decomposition to higher temperatures [12]. Higher Ag concentrations increase the transition temperature, indicating for thermal stability [13]. The present research has been focused mainly on synthesis of MnO_2-Ag nanocomposites in various ratios to assess their thermal stability to provide the data as baseline for end users for suitable applications.

2. Objectives

- To synthesize MnO_2–Ag nanocomposites in three different ratios (1:2, 1:1, and 2:1) using the hydrothermal method
- To characterize the synthesized nanocomposites and evaluate their thermal stability using Thermogravimetric Analysis (TGA) method
- To compare the thermal stability of MnO_2–Ag composites synthesized in ratios 1:2, 1:1 and 2:1 respectively
- To explain their electrical conductivity and its application as a catalytic component in electric storage batteries like Zinc Air Battery and as conducting materials in electronic devices.

3. Methods

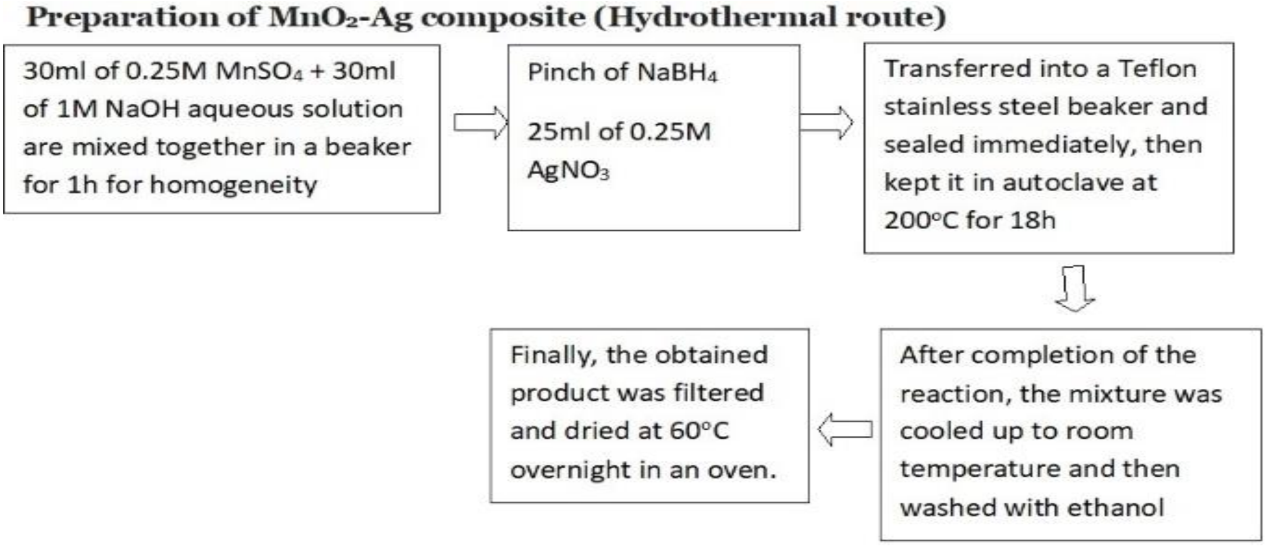
Synthesis of MnO_2-Ag Nanocomposite

3.1 Materials and Reagents used

All chemicals employed in this research programme were of analytical reagent (AR) grade. The primary materials included manganese sulphate ($MnSO_4$), sodium hydroxide (NaOH), sodium borohydride ($NaBH_4$), silver nitrate ($AgNO_3$), ethanol, and distilled water.

3.2 Hydrothermal Method

MnO_2–Ag nanocomposites (NCs) were synthesized by using the Hydrothermal method in three different ratios: 1:2, 1:1, and 2:1 respectively. In this method 30 mL of 0.25 M $MnSO_4$ solution is mixed with 30 mL of 1 M NaOH aqueous solution in a beaker to precipitate Manganese Hydroxide and sodium sulphate. The resulting mixture was stirred by using a magnetic stirrer for 1 hour to ensure homogeneity for the formation of $Mn(OH)_2$ and Na_2SO_4. A small quantity of $NaBH_4$ was added to the mixture as a reducing agent. The formed solution was divided into three portions. To each portion, 25 mL of 0.25 M $AgNO_3$ solution was added dropwise with different proportions to prepare MnO_2–Ag nanocomposites viz., Composite B-1: MnO_2: Ag (1:2), Composite B-2: MnO_2:Ag (1:1), Composite B-3: MnO_2: Ag (2:1) respectively. Each sample mixture transferred to a Teflon-lined stainless-steel autoclave and was sealed, and heated to 200 °C for 18 hours. After the completion of the hydrothermal reaction, the autoclaves were allowed to cool to room temperature. The precipitates formed were thoroughly washed with ethanol and then with double distilled water to discard any residual impurities formed if any. The Nanocomposites formed were filtered and dried in a hot air oven at 60°C for 12hours. The MnO_2–Ag Nanocomposites formed were collected and used for characterization. The materials Manganese sulphate ($MnSO_4$), Sodium Hydroxide (NaOH), Sodium Borohydride ($NaBH_4$), Silver Nitrate ($AgNO_3$), Ethanol used are of AR grade with double distilled water. The Hydrothermal Method explained as a flow chart presented here under:



Preparation of MnO_2-Ag composite (Hydrothermal route)

30ml of 0.25M $MnSO_4$ + 30ml of 1M NaOH aqueous solution are mixed together in a beaker for 1h for homogeneity

Pinch of $NaBH_4$

25ml of 0.25M $AgNO_3$

Transferred into a Teflon stainless steel beaker and sealed immediately, then kept it in autoclave at 200°C for 18h

After completion of the reaction, the mixture was cooled up to room temperature and then washed with ethanol

Finally, the obtained product was filtered and dried at 60°C overnight in an oven.

The composite samples MnO_2 :Ag (1:2), MnO_2 : Ag (1:1) and MnO_2: Ag (2:1) are presented in Fig (1).

Fig.1. MnO_2:Ag (2:1) ,MnO_2:Ag (1:1), MnO_2:Ag (1:2)

3.3 Thermal Stability of Nanocomposites:

Thermo Gravimetric Analysis (TGA) assessed the Thermal stability of Nanocomposites. The analysis was performed by using a TGA instrument (Make: Waters, TA Division; Model: Q50 V20.13 Build 39; Serial No: 0050-1493). The Ramp method employed in the temperature range from 20°C to 600°C at a ramp rate of 20°C/min, under the air environment.

4. Results

The thermograms for all three MnO_2-Ag nanocomposite samples are presented in Figures (1,2,3) respectively.In Figure 2, the Thermogram depicts the weight loss of a sample as a function of temperature, and can reveal its thermal stability. The initial weight loss (~0.47%) between 30°C and 105°C is attributed to the evaporation of moisture or volatile components. A secondary Weight loss (~4.72%) observed between 105°C and 332.4°C may be due to the decomposition of organic compounds if any or moisture content. A lower weight loss (~3.37%) observed between 332.4°C and 590°C, indicating thermal degradation of residual material at the end. This data can provide a clear understanding about the Nanocomposite B-1 with 1:2, which can explain the thermal behaviour, composition, and its degradation.

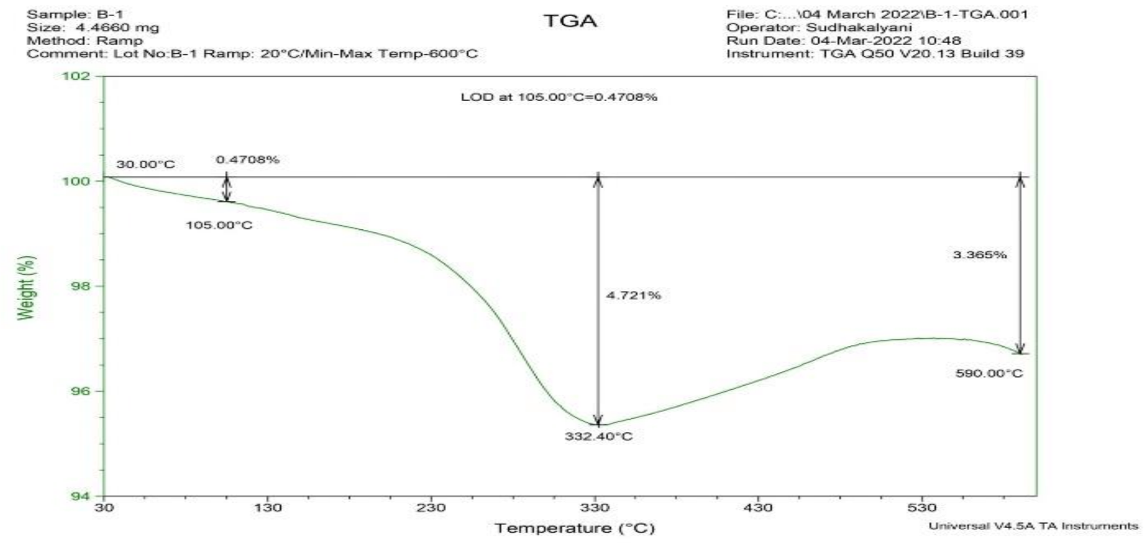


Figure 2: TGA Analysis of Sample B-1

In Figure 3, the Thermogram for B-2 sample shows the initial weight loss (~0.47%) between 30°C and 105°C, which indicates the evaporation of moisture or volatile components if any. A secondary weight loss (~1%) was observed at ~255°C, which may be due to the decomposition of organic compounds. A lower weight loss (~1.64%) was observed at 590°C, indicating thermal degradation of residual material at the end. This data can provide a clear understanding about the Nanocomposite B-2 with 1:1, which can explain the thermal behaviour, composition, and its degradation.

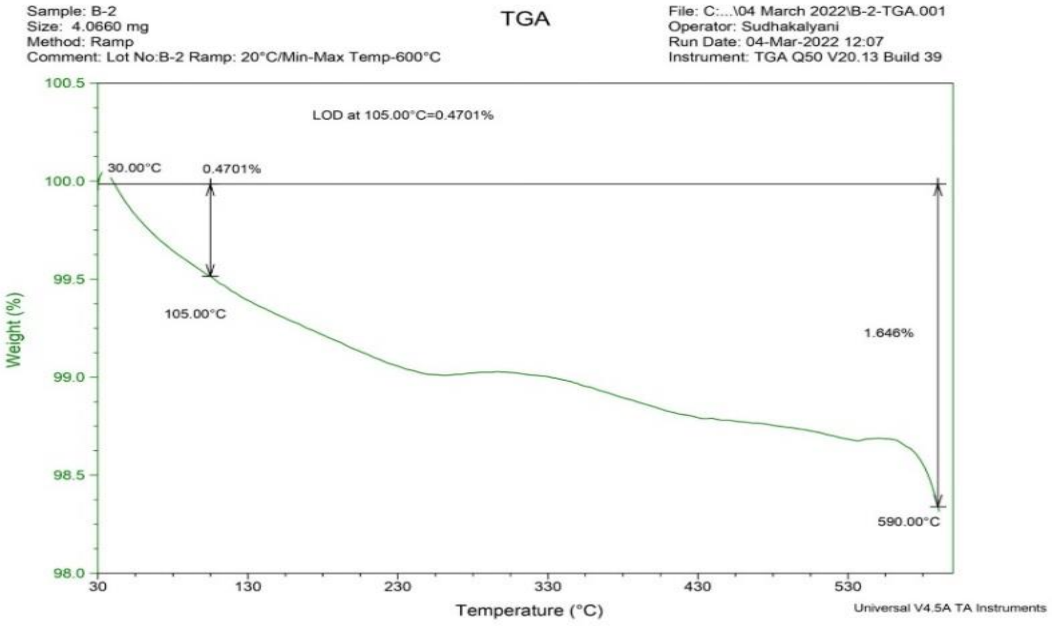


Figure 3: TGA Analysis of Sample B-2

In Figure 4, the Thermogram for the B-3 sample shows the initial weight loss (~0.45%) between 30°C and 105°C, which indicates the evaporation of moisture or volatile components, if any. A secondary weight loss (~0.92%) was observed at
220°C, which may be due to the decomposition of organic compounds. A lower weight loss (~2.07%) was observed at 590°C, indicating thermal degradation of residual material at the end. This data can provide a clear understanding of the Nanocomposite B-3 with 2:1, which can explain the thermal behaviour, composition, and its degradation.

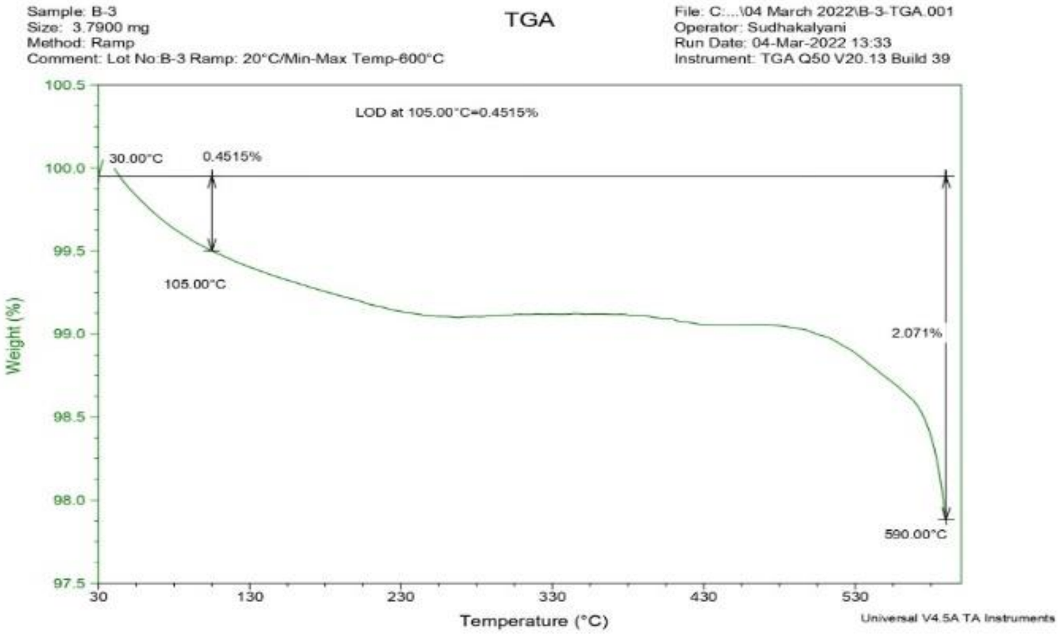


Figure 4: TGA Analysis of Sample B-3

Sample	Initial Weight Loss at 105 °C	Secondary Weight Loss temperature (%) 105°C-500°C	Secondary Weight Loss (%) 105°C-500°C	Final Weight Loss (%) at 590 °C	Total Weight Loss (%)	Thermal Stability
B-1	0.47%	~332 °C	4.72%	3.37%	8.56%	Stability-Low
B-2	0.47%	~255 °C	~1%	1.64%	2.12%	Stability-High
B-3	0.45%	~220 °C	~0.92%	2.07%	2.52%	Stability-Moderate

Table 1: Comparative Thermal Analysis of Samples B-1, B-2, and B-3

5. Discussion

In case of composite B-1 the net weight loss observed is 8.56% indicating its lower thermal stability. In case of B-3 the net weight loss 2.52% indicating its moderate thermal stability but in case of composite B-2 the net weight loss is found to be 2.12% indicating the composites higher thermal stability.

Increasing order of weight loss:

B-2 (2.12%)<B-3(2.52%)<B-1(8.56%)

The order of thermal stability

B-1<B-3<B-2

Based on the above facts the thermal stability of composite B-2 is comparatively higher than the other composites B-1 and B-3 respectively.

The nanocomposite B-1(1:2) is less thermally stable,which can create disruption in its structure or it can form layers of insulation,and in turn, its electrical conductivity decreases.Hence the composite will have lower electrical conductivity and making it as a suitable component in electrical storage batteries like Zinc Air batteries.

Generally, in most metals electrical conductivity decreases with increase in temperature but in semiconductor and composites, electrical conductivity increases with temperature.In B-2 the thermal stability is observed to be higher and in the case of B-3 thermal stability is somewhat nearer to B-2 and stands at a moderate level. Hence in composites B-2 and B-3 at elevated temperatures (590°C),electrical conductivity increases and hence these materials can be considered for suitable use as conducting materials in various electronic devices based on the need by the concerned manufacturing industrial personnel from time to time.

6. Conclusion

Metal Oxide –Metal nanocomposites play an important role due to their unique and potential characteristics. The nanocomposites MnO_2–Ag are synthesized with ratios 1:2,1:1 ,2:1 and assessed for their thermal stability. The nanocomposite B-1(1:2) due to its lower thermal stability, electrical conductivity also decreases and will have its application as a catalytic component in electric storage batteries like Zinc Air Battery. The nanocomposite MnO_2–Ag with ratio 1:1(B-2) and 2:1(B-3) has higher and moderate thermal stabilities respectively due to which electrical conductivity increases and can have application as a conducting material by end user in various electronic devices.

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