

# **Synthesis of Mn-based nanoparticles through polyol process under solvothermal conditions**

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## Abstract

Manganese-based nanoparticles (NPs) constitute a versatile class of inorganic materials with significant potential in catalysis, energy storage, and biomedical applications. In this study, a systematic investigation into the polyol-mediated solvothermal synthesis of Mn-based NPs with diverse compositions—including  $\text{MnCO}_3$ ,  $\text{MnOHCO}_3$ , and mixed-valence manganese oxides—is presented. Using polyols of distinct physicochemical properties (propylene glycol, PG, and tetraethylene glycol, TEG), various manganese precursors ( $\text{KMnO}_4$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mn}(\text{acac})_2$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ), and both organic and inorganic reducing agents (oleylamine, OAm; NaOH), we elucidate the influence of precursor chemistry and reaction environment on nanoparticle formation. Structural, morphological, and compositional analyses (XRD, TEM/SEM-EDS, FTIR, TGA, DLS, and UV–Vis spectroscopy) reveal controlled synthesis of phase-pure  $\text{MnCO}_3$ ,  $\text{MnOHCO}_3$ , and  $\text{Mn}_2\text{O}_3/\text{MnO}_2$  nanoparticles with distinct nanostructures and organic surface coatings derived from polyol oxidation products. Notably,  $\text{MnOHCO}_3$  nanoparticles are successfully synthesized for the first time, highlighting the crucial role of hydroxyl incorporation promoted by NaOH. The optical, colloidal, and thermochemical properties further underscore the suitability of these nanomaterials for semiconductive, catalytic, and biomedical applications. Overall, this work provides fundamental insights into the polyol solvothermal synthesis mechanism and introduces  $\text{MnOHCO}_3$  as a new Mn-based nanomaterial with promising potential for future technological applications.

## 1. Introduction

Inorganic nanoparticles (NPs) have emerged as a remarkable class of materials with multifaceted applications in various scientific and technological fields, including catalysis, energy storage, and biomedical applications.<sup>1-5</sup> Among the transition metal NPs, manganese-based, most commonly manganese oxide ( $\text{Mn}_x\text{O}_y$ ) and manganese carbonate ( $\text{MnCO}_3$ ) NPs, exhibit exceptional potential due to their unique properties, such as high magnetic susceptibility, catalytic activity, biocompatibility and strong adsorption capacity. Therefore, the synthesis of these NPs has commanded substantial attention in recent research endeavors<sup>6-10</sup>.

Manganese oxide NPs are a versatile class of nanomaterials with a rich array of properties and applications, including materials science<sup>11-13</sup>, environmental science<sup>14-16</sup>, and medicine<sup>8,17,18</sup>. Their chemical composition consists of various forms, including  $\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$ , each offering distinct properties and reactivity<sup>19,20</sup>. Notably,  $\text{Mn}_3\text{O}_4$  exhibits ferromagnetic behavior or superparamagnetic behavior at the nanoscale<sup>21,22,23</sup>, that can be exploited in applications like magnetic data storage<sup>24</sup> and targeted drug delivery<sup>25</sup>. These NPs also showcase diverse electrical conductivity based on their crystal structure and oxidation state<sup>26</sup>, with  $\text{MnO}_2$  NPs being used in supercapacitors and batteries due to their high electrical conductivity<sup>11,27,28</sup>. Moreover, they possess high catalytic activity in various chemical reactions<sup>8,29</sup>, including oxidation and reduction processes<sup>30,31</sup>, and high adsorption capacity<sup>32,33</sup>. Their optical properties, including fluorescence and UV-visible absorption, are harnessed in sensing applications and in combination with their biocompatibility they can be used in potential applications in drug delivery and biomedical imaging<sup>34-36</sup>.

In general, most manganese oxides are self-therapeutic<sup>6,8</sup>. Particularly, among the three oxidation states of manganese,  $\text{Mn}^{2+}$  ions show the best stability due to the semi-substituted outer 3d orbitals. As a result,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions possess oxidation capacity and can react with intracellular reducing substances, such as GSH, whereby participating in redox reactions they are reduced to  $\text{Mn}^{2+}$  and glutathione is oxidized. This interaction of oxidative  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$  with cells leads to intracellular depletion of GSH, which further affects several complex biochemical reactions. At the same time, different valence states of manganese exhibit different magnetism, specifically low valence manganese ions exhibit better relaxivity  $r_1$  due to more uncoupled electrons. Thus,  $\text{Mn}^{2+}$  ions show the strongest  $r_1$  relaxivity and are ideal candidates for MRI<sup>8,37</sup>.

Manganese carbonate ( $\text{MnCO}_3$ ) is an environmentally friendly material that is found in abundance on earth and at the same time possesses low toxicity and high biocompatibility<sup>9,38</sup>. In particular, the low

valence (+2) state of  $\text{MnCO}_3$  facilitates the insertion/removal of hydroxyl ions to form  $\text{MnOHCO}_3$  through electrochemical reaction, leading to manganese-rich valence states ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Mn}^{4+}$ , etc.). This property as well as high electrochemical active centers, rich Faradaic redox process and low cost make it a new emerging material for innumerable applications in the field of electrochemical devices and catalysts, such as electrodes for supercapacitors as well as batteries. The stabilization of the octahedral  $[\text{MnO}_6]$  structure due to the carbonate planes in the structure of rhodochrosite can also be beneficial for the occurrence of electrochemical reactions mainly on the electrode surface and endow longer cyclic lifetime as a pseudocapacitor<sup>38-40</sup>. Moreover,  $\text{MnCO}_3$  NPs can act as effective  $T_1$  contrast agents in magnetic resonance imaging by producing  $\text{Mn}^{2+}$  ions, which are simultaneously sensitive to acidic conditions further increasing the sensitivity in diagnosis. In parallel, under ultrasound irradiation they can efficiently produce hydroxyl radicals ( $\cdot\text{OH}$ ) and singlet oxygen ( $^1\text{O}_2$ ) while releasing  $\text{CO}_2$  and  $\text{Mn}^{2+}$  due to the degradation they undergo when in the local acidic tumor microenvironment. These properties make  $\text{MnCO}_3$  NPs an attractive material for biological applications such as drug delivery and imaging<sup>41-43</sup>. Lastly,  $\text{MnCO}_3$  provides an important and powerful precursor for the synthesis of manganese oxides through high temperature calcination process<sup>9,38,40</sup>.

Herein, we present a comprehensive investigation into the synthesis of Mn-based NPs with diverse compositions such as  $\text{Mn}_x\text{O}_y$ ,  $\text{MnCO}_3$  and  $\text{MnOHCO}_3$ , utilizing the polyol process under solvothermal conditions. The synthesis method explored involves the reduction of manganese precursors in a polyol medium via solvothermal treatment at elevated temperatures. The polyol process is an effective method for producing NPs with precise control over size, shape, and composition and can also lead to the formation of biocompatible organic coatings. The mechanism of the polyol process comprises of redox, complexation and decomposition reactions with the cations and anions of the solution. The products of the redox reactions are oxidized derivatives of polyols, like glycolaldehyde, glyoxylic acid, glycolic acid, oxalic acid, oxalates and even  $\text{CO}_2$ <sup>44-46</sup>. Solvothermal conditions, involving a combination of high temperature and pressure, further enhance the versatility and efficiency of this synthetic approach, allowing for the synthesis of high-quality products<sup>47</sup>. On that basis, glycols of different physicochemical properties such as 1,2-propylene glycol (PG) and tetraethylene glycol (TEG), manganese precursors of dissimilar redox potential and activity ( $\text{KMnO}_4$ ,  $\text{Mn}(\text{acac})_2$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  &  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ) and diverse type of reducing agents (organic, oleylamine (OAm) & inorganic, NaOH), have been employed. The resulting NPs will be characterized using a suite of advanced analytical techniques to assess their size, morphology, crystallinity, composition, and surface properties.

In general, this study aims to contribute to our understanding of the factors influencing the formation and properties of Mn-based NPs, which will be pivotal in tailoring their properties for specific applications. Also, the  $\text{MnOHCO}_3$  NPs, which were successfully synthesized for the first time in our study, introduce a novel NP type that opens doors to transformative breakthroughs in diverse fields, from materials science to medicine.

## 2. Materials and methods

*Chemicals and reagents:* All the reagents were of analytical grade and were used directly without further purification: potassium permanganate ( $\text{KMnO}_4$ ) (Aldrich,  $\geq 99.9\%$ ,  $M = 158.03 \text{ g/mol}$ ), manganese (II) acetylacetonate ( $\text{Mn}(\text{acac})_2$ ) (Aldrich,  $\geq 99.9\%$ ,  $M = 253.15 \text{ g/mol}$ ), manganese (II) chloride tetrahydrate ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) (Merc,  $\geq 99.9\%$ ,  $M = 253.15 \text{ g/mol}$ ), manganese (II) nitrate hydrate ( $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ ) (Aldrich,  $\geq 98\%$ ,  $M = 178.95 \text{ g/mol}$  (anhydrous basis)), oleylamine (OAm) (J & K Scientific,  $\geq 70\%$ ,  $M = 267.5 \text{ g/mol}$ ), 1,2-propylene glycol (PG) (Merck,  $\geq 99\%$ ,  $M = 76.10 \text{ g/mol}$ ), tetraethylene glycol (TEG) (Merck,  $\geq 99\%$ ,  $M = 194.23 \text{ g/mol}$ ), dimethyl sulfoxide (DMSO) (Aldrich,  $M = 78.13 \text{ g/mol}$ )

### 2.1. Synthesis of Mn-based NPs

**Sample Mn1:** 0.2 g  $\text{KMnO}_4$  (1.26 mmol) was dissolved in 8 mL of PG, and mixed well under stirring at 30 °C for 15 min. The supernatant was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process. The reaction was carried out at 200 °C for 24 h, followed by natural cooling to room temperature. Afterward, the synthetic mixture was centrifuged at 5000 rpm for 20 min and washed three times with disolol, where the supernatants were discarded and a brown precipitate was acquired. The reaction yield was calculated at 5.45% based on the metal precursor.

**Sample Mn2:** 0.2 g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.79 mmol) was dissolved in 2 mL of PG (solution 1). 2 mL of PG was mixed with 4 mL of OAm (solution 2). Both solutions were mixed well under stirring at 30 °C for 5 min. Afterwords the solution 2 was added to the solution 1 and was mixed well under stirring at 30 °C for another 10 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process. The reaction was carried out at 200 °C for 24 h, followed by natural cooling to room temperature. The reaction yield was calculated at 29.95% based on the metal precursor.

Sample **Mn3**: 0.2 g  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.79 mmol) was dissolved in 4 mL of PG. 0.2 g of NaOH was dissolved in 4 mL of PG (solution 2). Both solutions were mixed well under stirring at 30 °C for 5 min. Afterwards the solution 2 was added to the solution 1 and was mixed well under stirring at 30 °C for another 10 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process at 200 °C for 24 h. The reaction yield was calculated at 35.55% based on the metal precursor.

Sample **Mn4**: 0.2 g  $\text{KMnO}_4$  (1.26 mmol) was dissolved in 8 mL of TEG, and mixed well under stirring at 30 °C for 15 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process at 200 °C for 24 h. The reaction yield was calculated at 58.25% based on the metal precursor.

Sample **Mn5**: 0.2 g  $\text{Mn}(\text{acac})_2$  (1.11 mmol) was dissolved in 4 mL of TEG. 0.2 g of NaOH was dissolved in 4 mL of TEG (solution 2). Both solutions were mixed well under stirring at 30 °C for 5 min. Afterwards the solution 2 was added to the solution 1 and was mixed well under stirring at 30 °C for another 10 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process at 200 °C for 24 h. The reaction yield was calculated at 30% based on the metal precursor.

Sample **Mn6**: 0.2 g  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (1.12 mmol) was dissolved in 8 mL of TEG, and mixed well under stirring at 30 °C for 15 min. The resulting solution was transferred into a Teflon-lined stainless-steel autoclave to set out a solvothermal polyol process. The reaction was carried out at 200 °C for 24 h, followed by natural cooling to room temperature. The reaction yield was calculated at 23.9% based on the metal precursor.

It is important to highlight that the inclusion of an extra reducing agent was considered essential. This addition is crucial as, in its absence, the system results in the formation of soluble manganese compounds instead of nanoparticles. To elaborate, when 0.2 g of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  was combined with 8 mL of PG without the incorporation of a reducing agent, soluble compounds of manganese and PG were synthesized.

## **2.2. Characterization**

The crystal structure and crystallite size of synthesized NPs were investigated through X-ray diffraction (XRD) ... performed in the  $2\theta$  region from 10 to  $90^\circ$ , with monochromatized Cu-K $\alpha$  radiation ( $\lambda = 1.5418$  Å). The chemical information of the NPs was determined by Fourier transform infrared spectroscopy (FT-IR) using Nicolet 6700 FT-IR spectrometer in the wavenumber range of 4000-400  $\text{cm}^{-1}$  (2  $\text{cm}^{-1}$  resolutions; 30 scans). Transmission Electron Microscopy (TEM) images were obtained .... The morphology of the NPs was determined by a JEOL 840A scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometry (EDX) for estimating their elemental composition. Thermogravimetric analysis (TGA) was employed using SETA-RAM SetSys-1200 instrument and performed at a heating rate of 10  $^\circ\text{C}/\text{min}$  from room temperature to 900  $^\circ\text{C}$  under nitrogen atmosphere. UV/vis spectra were recorded with a Jasco V-750 double-beam UV/vis spectrophotometer. The hydrodynamic size and  $\zeta$ -potential were measured using a Nano ZS Malvern apparatus at room temperature.

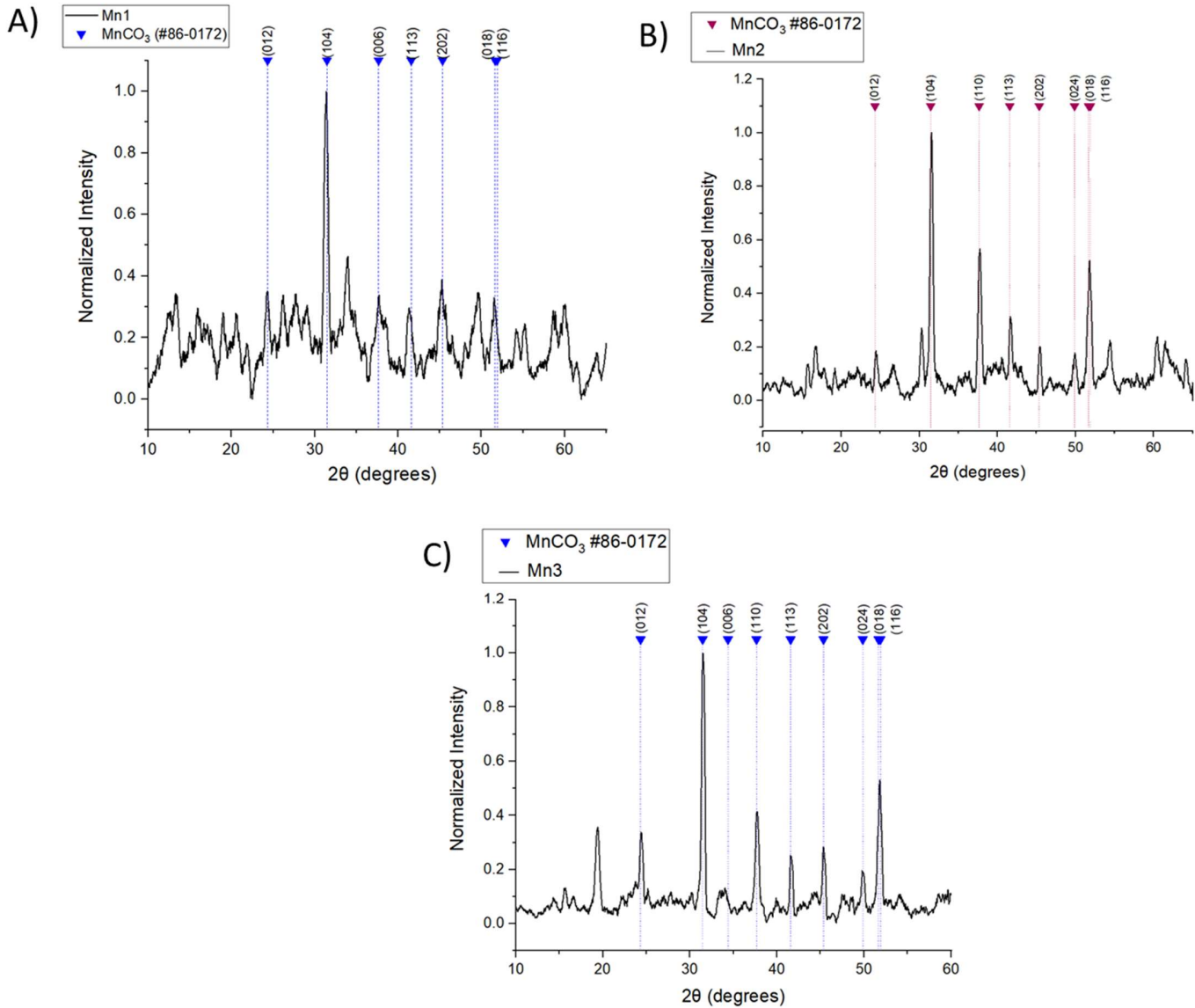
### 3. Results and Discussion

#### 3.1. Mn-based NPs synthesized with PG

**Figure 1** demonstrates the X-ray diffraction (XRD) graphs of the synthesized Mn-based NPs synthesized with PG. Starting with  $\text{KMnO}_4$  precursor and in the presence of PG (Fig.1A) resulted in the formation of hexagonal  $\text{MnCO}_3$  NPs with space group R-3c, as indicated by the diffraction peaks that correspond to the (012), (104), (006), (113), (202), (018) and (116) planes of  $\text{MnCO}_3$  rhodochrosite phase (JCPDS no. 86-0172)<sup>40</sup>. Lattice parameters were estimated at  $a = b = 4.773$  Å,  $c = 15.642$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ <sup>48,49</sup>. The absence of any additional peaks in the diffraction pattern serves as confirmation of the high purity of the manganese carbonate ( $\text{MnCO}_3$ ) crystallite.

In the case of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  precursor and in the presence of PG (Fig.1A, B), both reducing agents employed resulted also in the synthesis of hexagonal  $\text{MnCO}_3$  NPs as shown by the diffraction peaks that correspond to the (012), (104), (006), (110), (113), (202), (024), (018) and (116) planes of  $\text{MnCO}_3$  rhodochrosite phase (JCPDS no. 86-0172). Lattice parameters were estimated at  $a = b = 4.773$  Å,  $c = 15.642$  Å,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

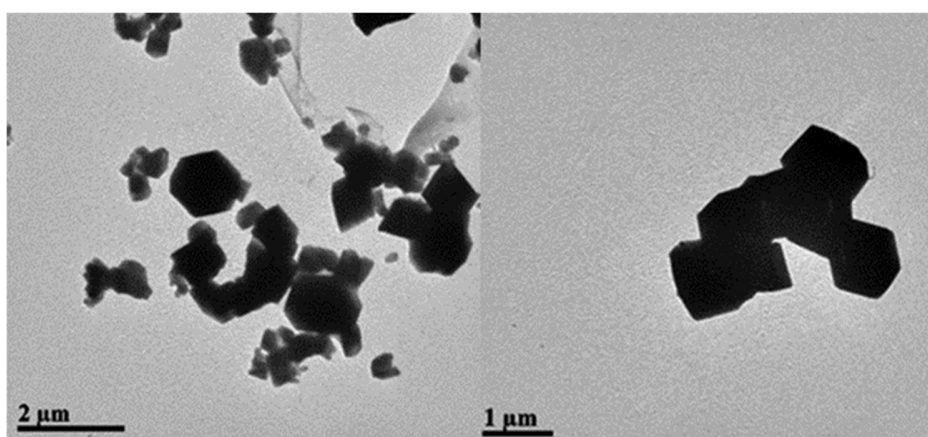
The crystallite size of all phases was calculated from the Scherrer equation,  $D = 0.891\lambda/\beta \cos\theta$ , and the full width at half-maximum of the main peak of each crystallite phase. For the  $\text{MnCO}_3$  phase of Mn1 the crystallite size is 26 nm, for Mn2 is 48 nm and for Mn3 is 38 nm, respectively.



**Figure 1.** X-ray diffraction graphs of Mn-based NPs (Mn1, Mn2, Mn3) synthesized with PG.

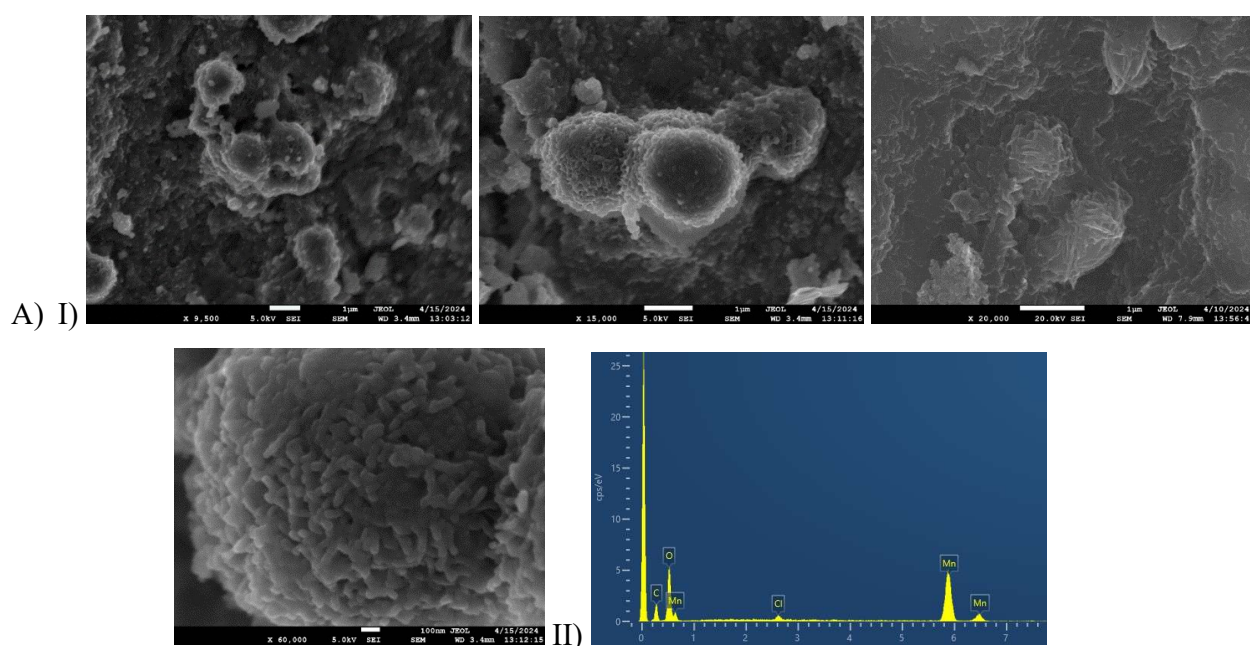
The morphology of the synthesized NPs was investigated with electron microscopy. TEM images are presented in **Figure 2**. The Mn2 NPs (Fig. 2) have a mainly cubic or hexagonal shape with varying size distribution, with a maximum size of 140 nm.



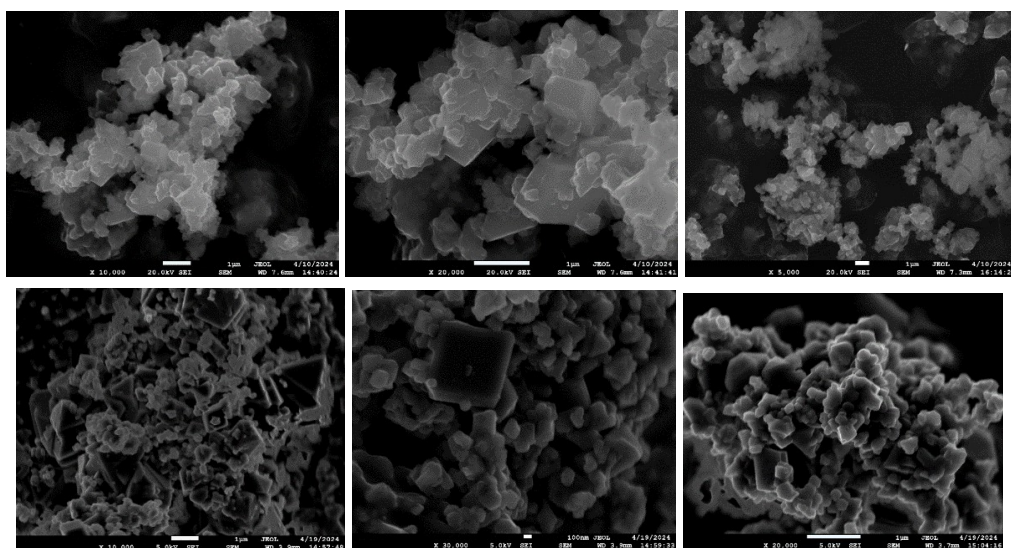


**Figure 2.** TEM images of Mn<sub>2</sub> NPs.

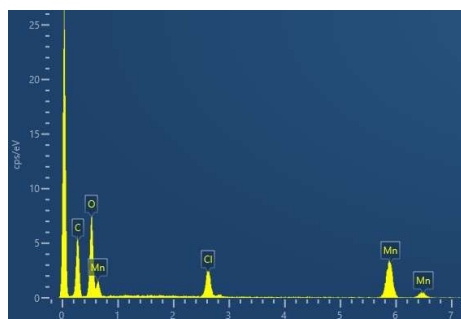
**Figure 3** demonstrates that Mn<sub>1</sub> NPs possess a spherical morphology. For Mn<sub>2</sub> Fig. 3B certifies their cubic or hexagonal shape of variable sizes. Mn<sub>3</sub> NPs have the morphology of hexagonal nanoplates with a broad size distribution. The energy-dispersive X-ray spectroscopy (EDS) analysis results, which reveal the presence of carbon (C) and manganese (Mn) elements, are depicted in Fig. 3(II).



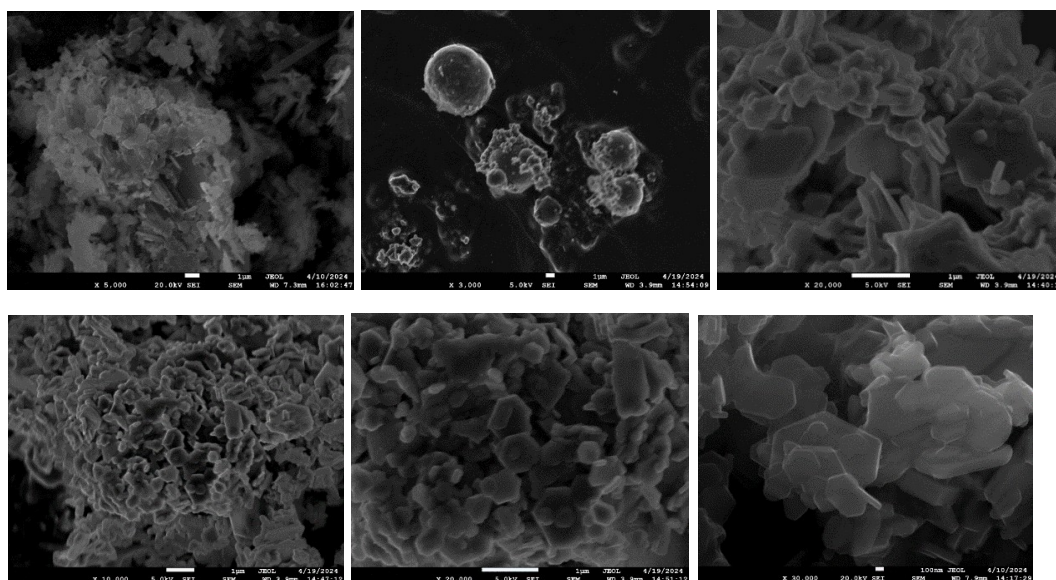
B) I)

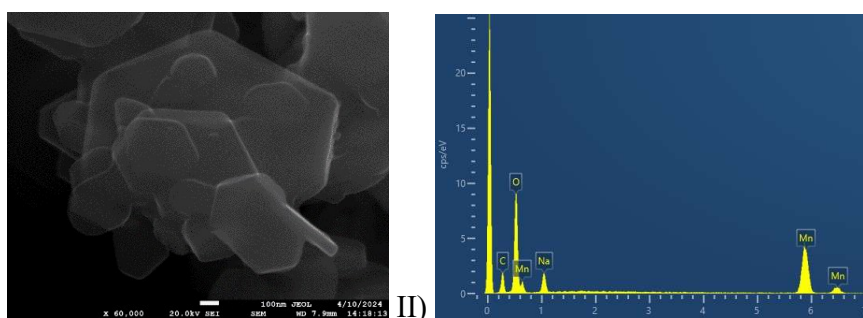


II)



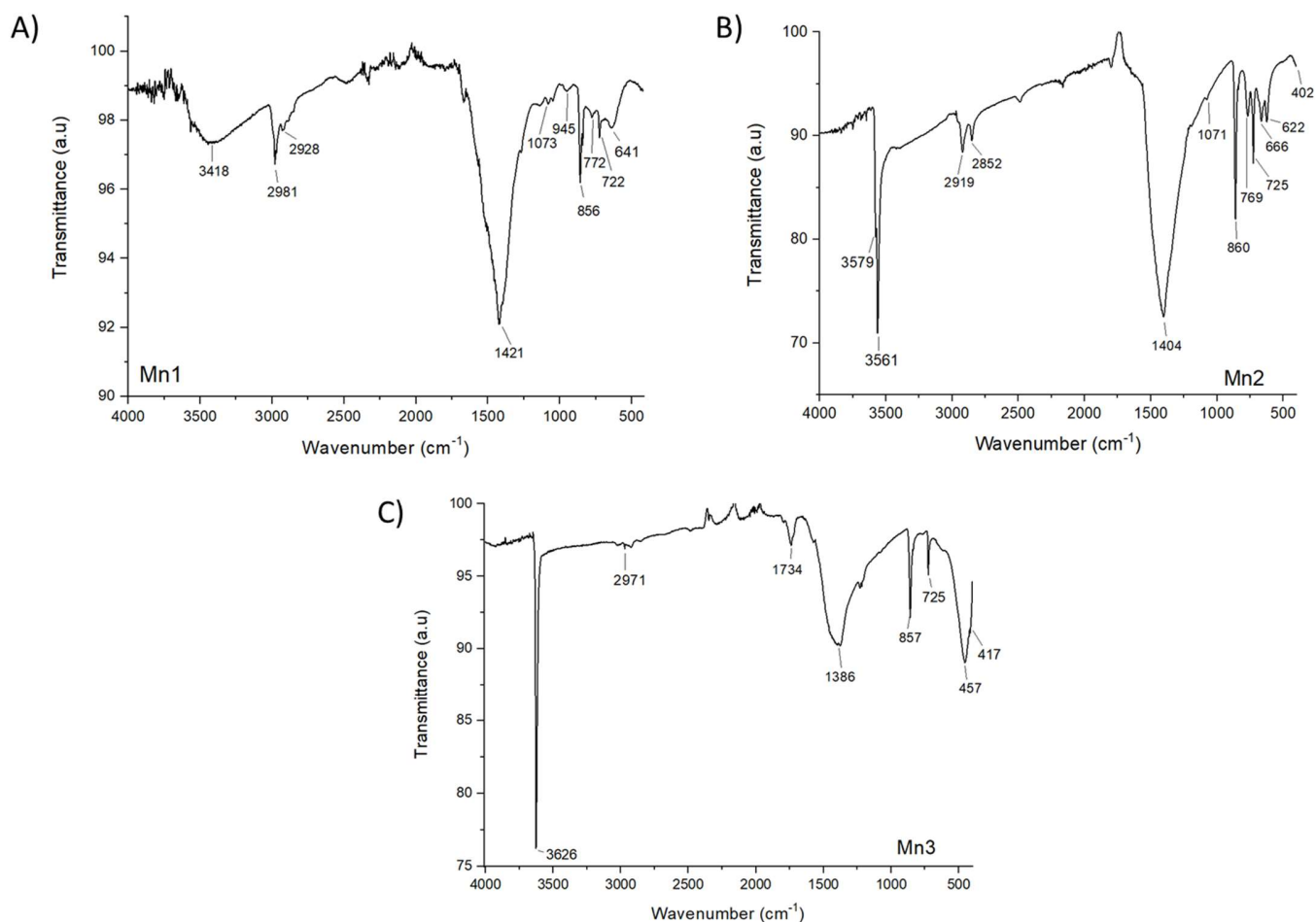
C) I)





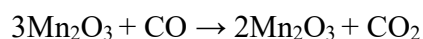
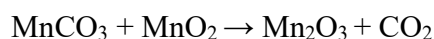
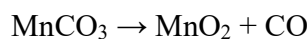
**Figure 3.** (I) SEM images of A) Mn1, B) Mn2, C) Mn3 NPs. (II) EDS spectra of A) Mn1, B) Mn2, C) Mn3.

The presence of the organic coating on the surface of the NPs has been confirmed by FTIR spectra (**Figure 4**). In the FT-IR spectrum of the Mn1 (Fig. 4A), the absorptions at 2981 and 2928  $\text{cm}^{-1}$  are attributed to the bending vibrations of methylene groups  $-\text{CH}$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ , derived from propylene glycol. The characteristic peaks at 1421, 860 and 722  $\text{cm}^{-1}$  are attributed to the vibrations of  $\text{CO}_3$  groups<sup>43</sup>. The absorption at 641  $\text{cm}^{-1}$  is attributed to the lattice vibrations of  $\text{Mn}-\text{O}$  bond<sup>9</sup>. In the spectrum of the Mn2 (Fig. 4B), the strong absorptions at 3579  $\text{cm}^{-1}$  and 3561  $\text{cm}^{-1}$  are attributed to the  $\text{N}-\text{H}_2$  bond, which confirms the existence of OAm on the surface of the NPs. Also, the absorptions at 2919 and 2852  $\text{cm}^{-1}$  are attributed to the bending vibrations of the methylene groups  $-\text{C}-\text{H}$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_3$ , which are derived from OAm<sup>50,51</sup>. The peaks at 1404, 860 and 725  $\text{cm}^{-1}$  are characteristic of the  $\text{CO}_3$  groups and the absorptions at 666 and 622  $\text{cm}^{-1}$  are attributed to the lattice vibrations of  $\text{Mn}-\text{O}$  bond. In the Mn3 spectrum (Fig. 4C) the characteristic peaks of the methylene groups vibrations, 2971  $\text{cm}^{-1}$ , and the peaks at 1734  $\text{cm}^{-1}$  and 1386  $\text{cm}^{-1}$  suggest the presence of the oxidation derivatives of PG on the surface of NPs. There are also evident the characteristic absorptions of the  $\text{CO}_3$  groups at 1404, 857 and 725  $\text{cm}^{-1}$  and of the  $\text{Mn}-\text{O}$  bond at 457 and 417  $\text{cm}^{-1}$ . The strong absorption at 3626  $\text{cm}^{-1}$  is allotted to the presence of hydroxyl anions and in combination to the lower intensity of the peak at 1404  $\text{cm}^{-1}$  suggest the adsorption of hydroxyl ions on the crystal lattice of  $\text{MnCO}_3$  and consequently the formation of  $\text{MnOHCO}_3$ .



**Figure 4.** IR spectra of Mn-based NPs (Mn1, Mn2, Mn3) synthesized with PG.

**Figure 5** shows the thermogravimetric curves of the NPs, presenting the weight loss in correlation to the temperature (25-900 °C). To investigate the percentage of carbon dioxide yielded by manganese carbonate, thermogravimetric analysis of bulk  $\text{MnCO}_3 \cdot x\text{H}_2\text{O}$  (Fig. 5A) (MB 114.95 g/mol, moisture content 43-46%) was performed. In general, manganese carbonate undergoes thermal decomposition when heated in a nitrogen atmosphere, yielding  $\text{CO}_2$  and  $\text{MnO}_2$  which is simultaneously converted to  $\text{Mn}_2\text{O}_3$ .  $\text{Mn}_2\text{O}_3$  remains thermally stable up to 900°C and then decomposes to form  $\text{Mn}_3\text{O}_4$ <sup>52</sup>.

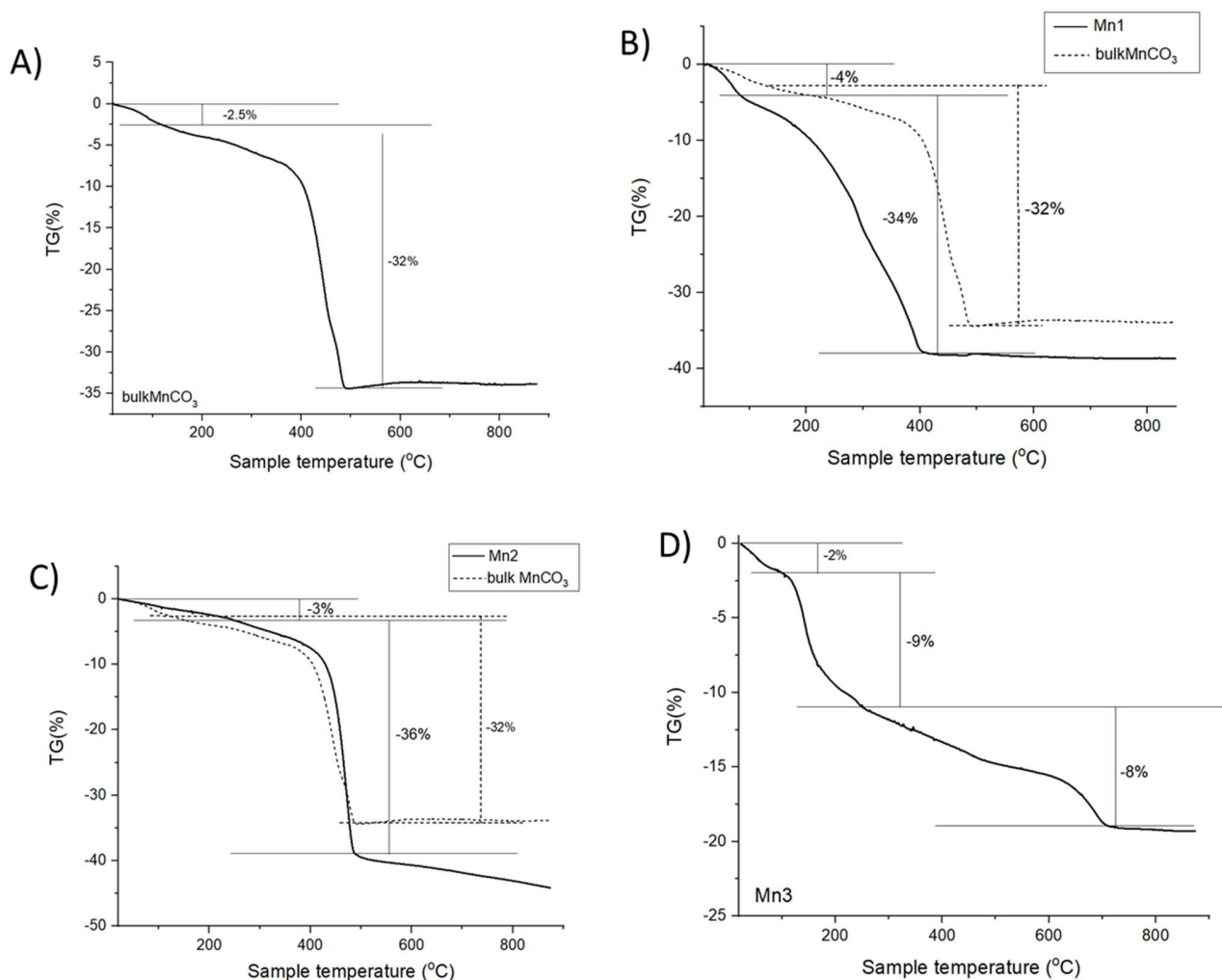


In Figure 5A, from 20 to 155 °C, a weight loss of 2.5% is observed due to the removal of the moisture in the sample. From 155 to 491 °C, a sharp weight loss of 32% is observed because of the manganese

carbonate which yields carbon dioxide ( $\text{CO}_2$ ) and forms manganese oxides, where an increase in mass is observed, an exothermic effect, due to the oxidation of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  to  $\text{Mn}_3\text{O}_4$ .

Initially, in the TGA curve of the  $\text{MnCO}_3$  NPs (Fig. 5B) a 4% weight loss is observed from 20 to 80 °C, due to the removal of adsorbed water in the sample. As the temperature increases, from 80 to 400 °C, there is a sharp weight loss of 34% due to the decomposition of a quantity of organic compounds as well as the decomposition of manganese carbonate which gives off carbon dioxide ( $\text{CO}_2$ ) and forms manganese oxides. The total weight loss of the NPs reaches 38% of its initial mass. Compared with the TGA curve of bulk  $\text{MnCO}_3$ , it can be concluded that most of the weight loss comes from the decomposition of carbonate ions and a small percentage comes from the presence of organic compounds on the surface of  $\text{MnCO}_3$  NPs. Also due to the nanoscale, the removal of organic compounds starts at lower temperatures and is finally completed at 400 °C compared to 500 °C of bulk  $\text{MnCO}_3$ . For the  $\text{MnCO}_3$  NPs with the OAm coating (Fig. 5C) an initial weight loss of 3% is evident, due to the removal of adsorbed water. As the heating continues, from 250 to 400°C, a sharp weight loss of 36% is recorded due to the decomposition of an amount of surfactant, oleylamine, which decomposes at 370 °C in nitrogen atmosphere<sup>53</sup>, as well as the decomposition of part of manganese carbonate. The total weight loss of the NPs reaches 39% of its original mass. Compared with the TGA curve of bulk  $\text{MnCO}_3$ , it can be concluded that the surfactant content is about 4% and the remaining percentage comes from the decomposition of carbonate ions. In the TGA curve of the  $\text{MnOHCO}_3$  NPs (Fig. 5D), an initial weight loss of 2% from 20 to 102 °C is observed, due to moisture in the sample. Thereafter, a gradual removal of organics is observed, from 100 to 250 °C there is a weight loss of 9% and from 250 to 710 °C a weight loss of 8% due to the decomposition of low molecular weight organics, hydroxyls and the release of carbon dioxide. The total weight loss of the NPs reaches 19% of its initial mass.

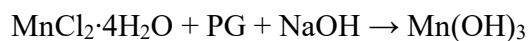


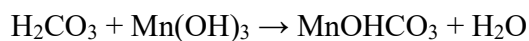


**Figure 5.** Thermogravimetric analysis (TGA) of Mn-based NPs (Mn1, Mn2, Mn3) synthesized with PG.

The structural composition and crystallite size of all synthesized NPs using PG are presented in **Table 1**. In the case of using PG and manganese source  $\text{KMnO}_4$  the system is driven to produce NPs of pure  $\text{MnCO}_3$ . This phenomenon arises because of the complete redox reaction that takes place, wherein Mn undergoes reduction from the +7 oxidation state to +2, while at the same time PG is completely oxidized to carbonate ions and a minor fraction remains in lower oxidation products.

The employment of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  as a manganese precursor, in conjunction with PG and the organic reducing agent OAm, results in coated  $\text{MnCO}_3$  NPs. In contrast, utilizing the inorganic reducing agent NaOH, results in the synthesis of  $\text{MnCO}_3$  NPs with hydroxyls in the crystal lattice, denoted as  $\text{MnOHCO}_3$ . The underlying chemical reactions are articulated as follows:





Where  $\text{Mn}(\text{OH})_3$  is formed as an intermediate which promotes the formation of  $\text{MnOHCO}_3$ .

**Table 1. Characterization of synthesized Mn-based NPs using PG.**

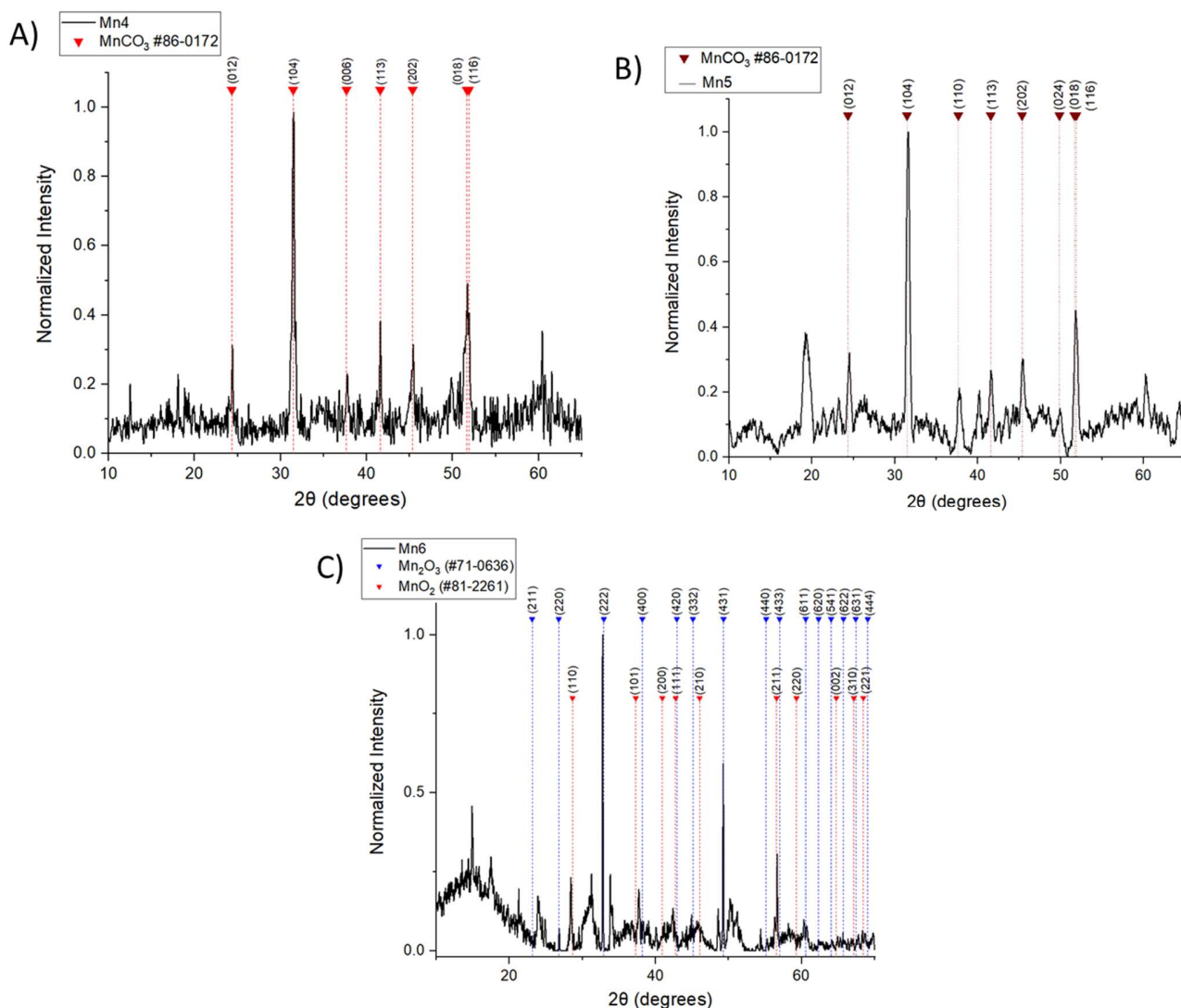
Sample name	Precursor	Polyol	Reducing agent	Composition	$d_{\text{XRD}}$ (nm)	Org. coating (% w/w)	Carbonate ions (%w/w)
Mn1	$\text{KMnO}_4$	PG	-	$\text{MnCO}_3$	26	2	32
Mn2	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	PG	OAm	$\text{MnCO}_3$	48	4	32
Mn3	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	PG	NaOH	$\text{MnOHCO}_3$	38		

### 3.2. Mn-based NPs synthesized with TEG

**Figure 6** demonstrates the X-ray diffraction (XRD) graphs of the synthesized Mn-based NPs synthesized with TEG.  $\text{KMnO}_4$  precursor and in the presence of TEG (Fig.6A) resulted in the synthesis of hexagonal  $\text{MnCO}_3$  NPs as shown from the diffraction peaks that correspond to the (012), (104), (006), (113), (202), (018) and (116) planes of  $\text{MnCO}_3$  rhodochrosite phase (JCPDS no. 86-0172). Lattice parameters were estimated at  $a = b = 4.773 \text{ \AA}$ ,  $c = 15.642 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ .

When using  $\text{Mn}(\text{acac})_2$  precursor in the presence of TEG and NaOH as a reducing agent (Fig.6B) resulted in the formation of hexagonal  $\text{MnCO}_3$  NPs as displayed by the diffraction peaks that correspond to the (012), (104), (110), (113), (202), (024), (018) and (116) planes of  $\text{MnCO}_3$  rhodochrosite phase (JCPDS no. 86-0172). Lattice parameters were estimated at  $a = b = 4.773 \text{ \AA}$ ,  $c = 15.642 \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ . In contrast,  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  in the presence of TEG (Fig.6C) lead to the synthesis of cubic phase bixbyite with space group Ia-3,  $\text{Mn}_2\text{O}_3$  NPs (92%) with traces of cubic phase pyrolusite,  $\text{MnO}_2$  (8%) as indicated by the diffraction peaks that correspond to the (211), (220), (222), (400), (420), (332), (431), (440), (433), (611), (620), (541), (622), (631) and (444) planes of  $\text{Mn}_2\text{O}_3$  bixbyite phase (JCPDS no. 71-0636) and (110), (101), (200), (111), (210), (211), (220), (002), (310) and (221) planes of  $\text{MnO}_2$  pyrolusite phase (JCPDS no. 81-2261). Lattice parameters were estimated at  $a = b = c = 9.4146 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  for  $\text{Mn}_2\text{O}_3$ <sup>54</sup>, and  $a = b = 4.4041 \text{ \AA}$ ,  $c = 2.8765 \text{ \AA}$ ,  $\alpha = \beta = \gamma = 90^\circ$  for  $\text{MnO}_2$ <sup>55</sup>.

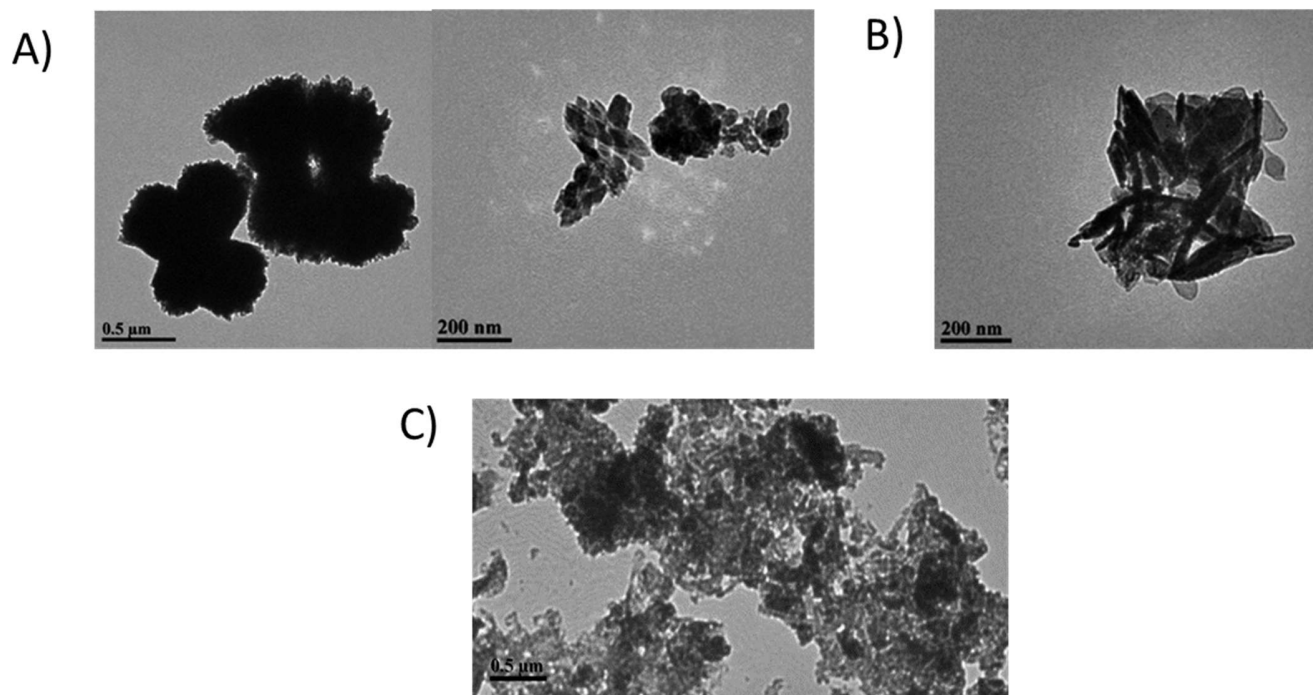
The crystallite size of Mn4 NPs was calculated 25 nm, of Mn5 41 nm and of the mixture  $\text{Mn}_2\text{O}_3/\text{MnO}_2$ , Mn6 NPs, 140 nm, respectively.



**Figure 6.** X-ray diffraction graphs of Mn-based NPs (Mn4, Mn5, Mn6) synthesized with TEG.

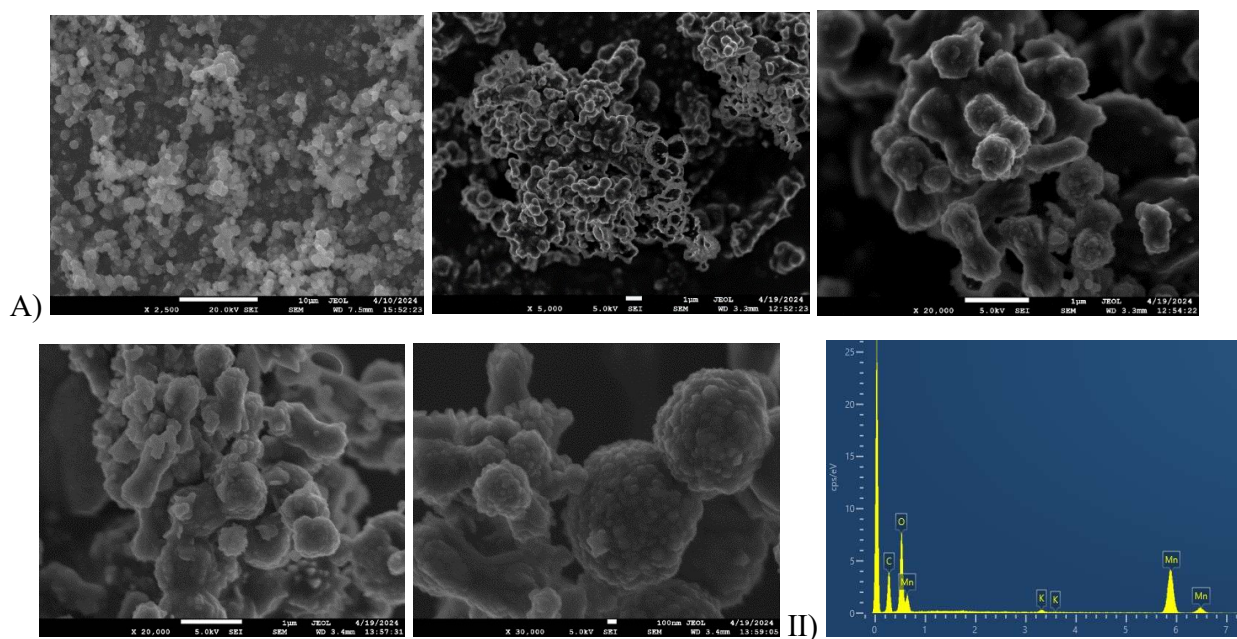
TEM images are presented in **Figure 7**. The Mn4 NPs (Fig. 7A) are located in clusters, which consist of rhombic-shaped nanoplates that form peanut-shaped aggregates with spiky edges. The Mn5 NPs (Fig. 7B) are in the form of clustered nanorods of varying size and roughness. Lastly, the Mn6 NPs (Fig. 7C) have no distinct shape and appear to have small size with irregular shape.



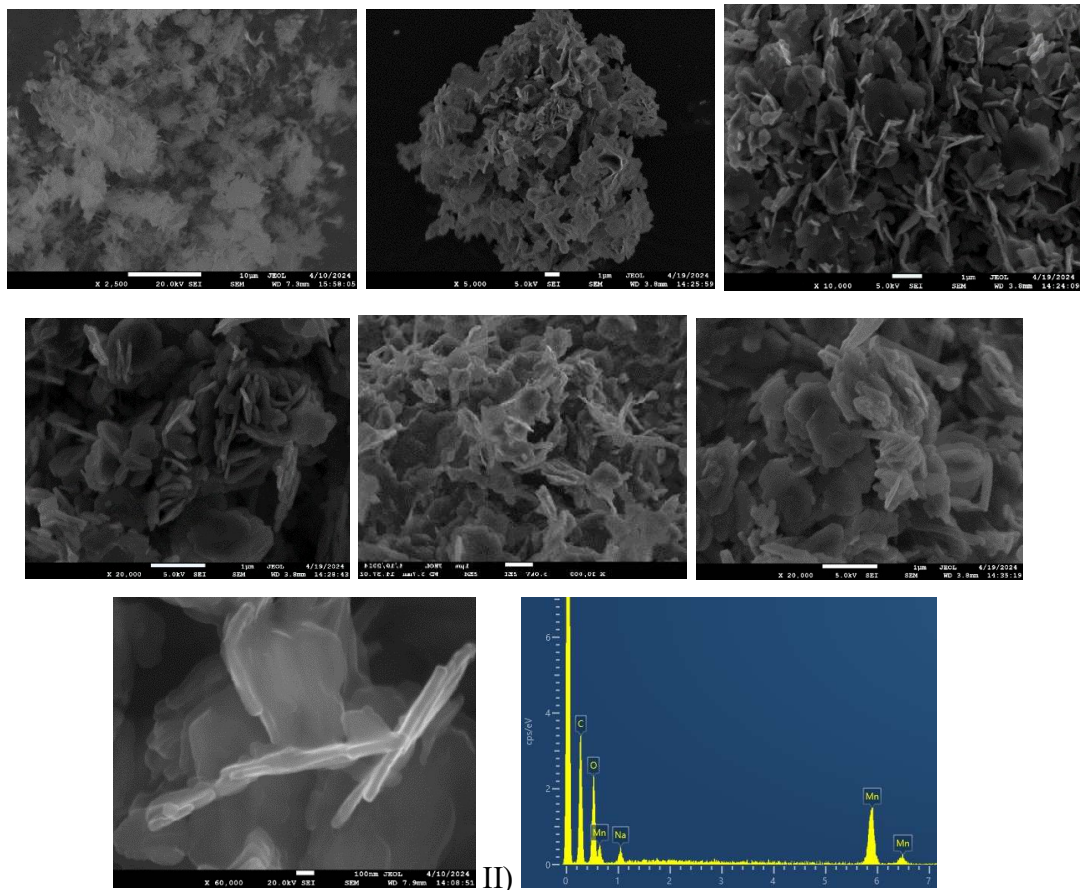


**Figure 7.** TEM images of Mn-based NPs (Mn4, Mn5, Mn6) synthesized with TEG.

**Figure 8** displays the peanut-shaped aggregates with irregular edges formed by Mn4 nanoparticles (NPs), while Fig. 8B shows the nanorod aggregates formed by Mn5. Mn6 NPs exhibit a spherical morphology, as shown in Fig. 8C. The energy-dispersive X-ray spectroscopy (EDS) analysis results, indicating the presence of carbon (C) and manganese (Mn) elements, are presented in Fig. 8(II).

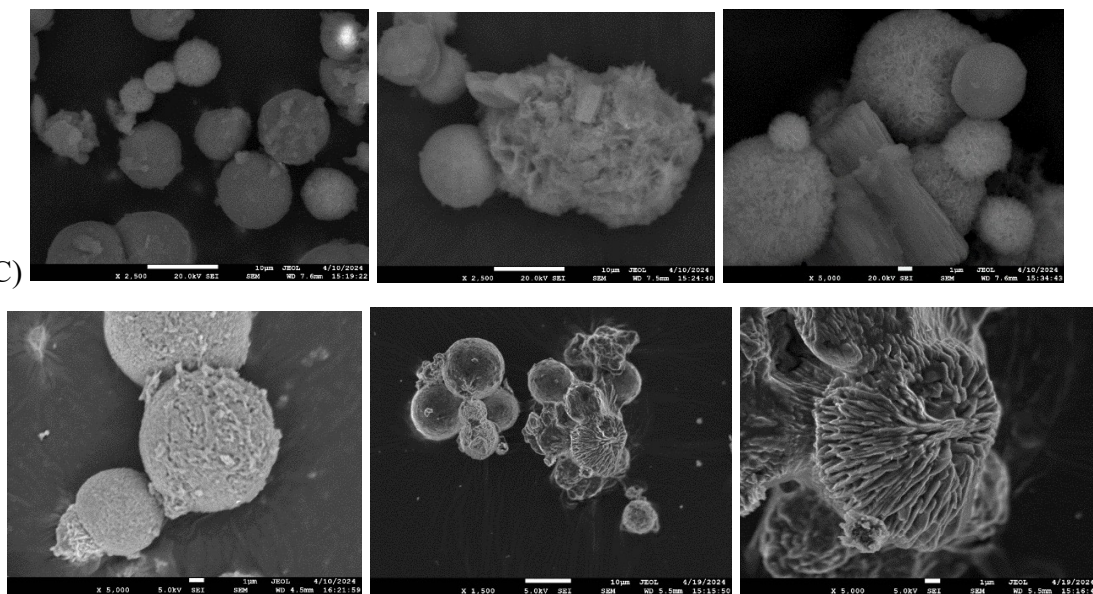


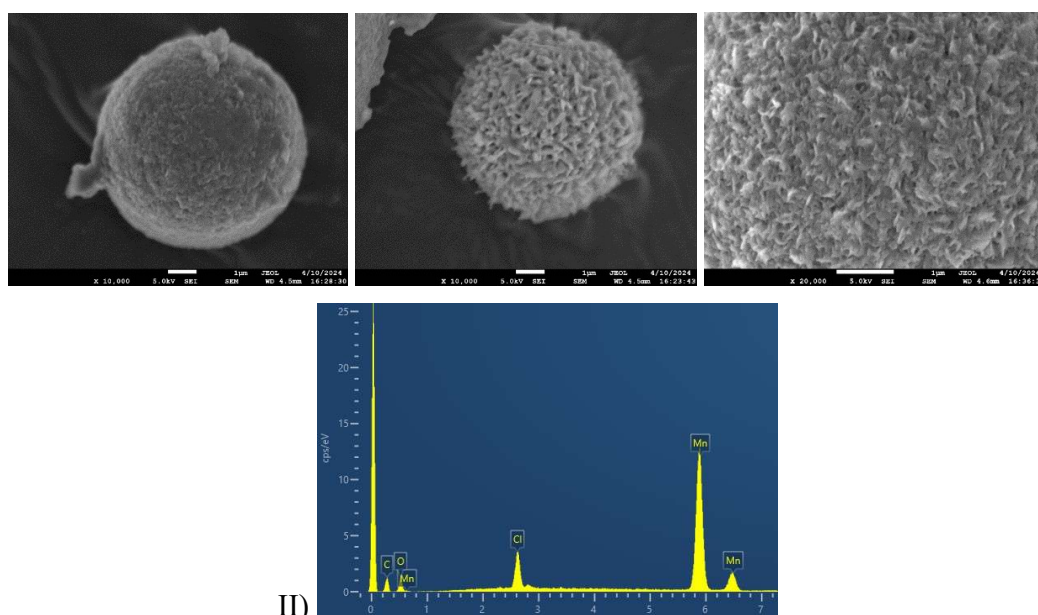
B)



II)

C)

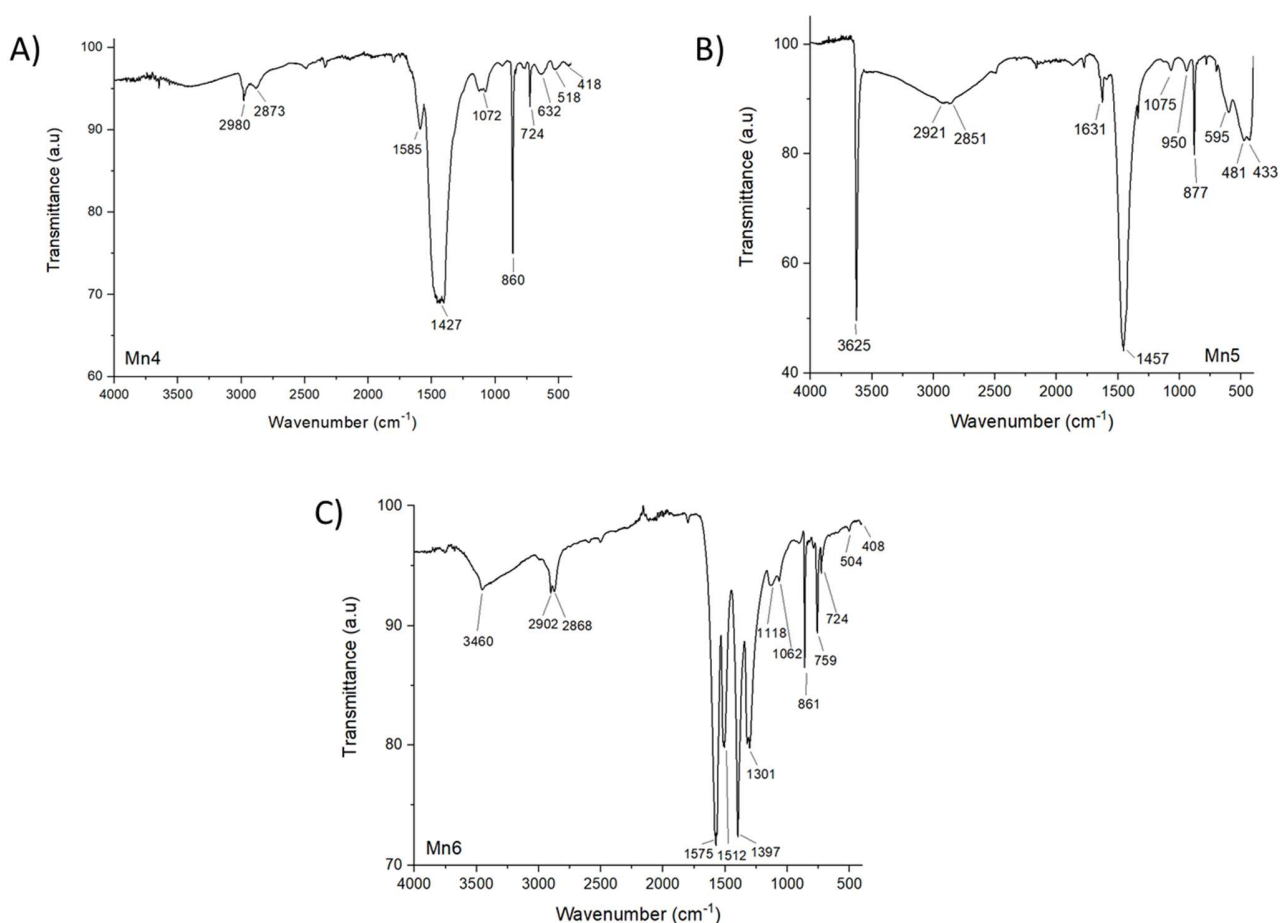




**Figure 8.** (I) SEM images of A) Mn4, B) Mn5, C) Mn6 NPs. (II) EDS spectra of A) Mn4, B) Mn5, C) Mn6.

**Figure 9** presents the FTIR spectra of the synthesized NPs in the presence of TEG. In the Mn4 spectrum (Fig. 9A) the absorptions at 2980 and 2873  $\text{cm}^{-1}$  are attributed to the methylene groups vibrations. The peak at 1585  $\text{cm}^{-1}$ , which corresponds to the vibrations of the C=O bond<sup>56</sup>, and the multiplicity of the peak at 1403  $\text{cm}^{-1}$  certify the presence of the oxidation derivatives of TEG on the surface of NPs. Moreover, the characteristic absorptions of the CO<sub>3</sub> groups at 1403, 860 and 724  $\text{cm}^{-1}$  and of the Mn-O bond at 632 and 518  $\text{cm}^{-1}$  are apparent. In the Mn5 spectrum (Fig. 9B) the strong peak at 3625  $\text{cm}^{-1}$  indicates the presence of hydroxyl anions and in combination to the presence of the characteristic absorptions of the CO<sub>3</sub> groups at 1457, 877 and 713  $\text{cm}^{-1}$  verify the formation of MnOHCO<sub>3</sub>. The peaks at 2921 and 2851  $\text{cm}^{-1}$  of the methylene groups vibrations and the peak at 1631  $\text{cm}^{-1}$  are attributed to the presence of the oxidation derivatives of TEG on the surface of NPs. Lastly, in the Mn6 spectrum (Fig. 9C) the broad band at 3460  $\text{cm}^{-1}$  is attributed to adsorbed water molecules. The peaks at 1118 and 1062  $\text{cm}^{-1}$  correspond to the C-O-C vibration and the absorptions at 861 and 759  $\text{cm}^{-1}$  are attributed to the in-plane C-H bond bending vibration, which are derived from TEG oxidation derivatives. The N-O bond stretching vibrations occur at 1575 and 1512  $\text{cm}^{-1}$  for the asymmetric N-O stretch and at 1397 and 1301  $\text{cm}^{-1}$  for the symmetric N-O stretch. The absorption at 504  $\text{cm}^{-1}$  is attributed to the vibrations of Mn-O bond.

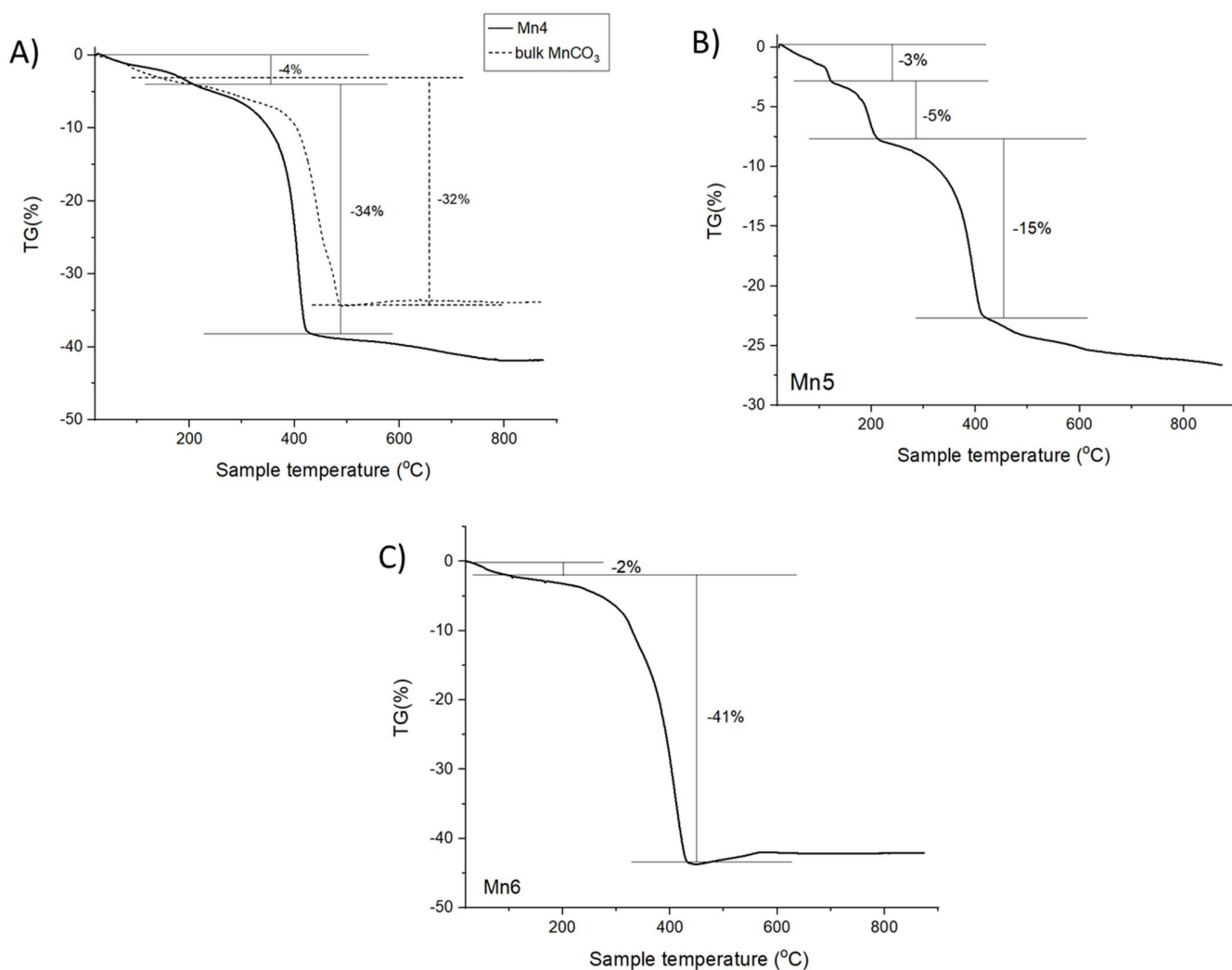




**Figure 9.** IR spectra of Mn-based NPs (Mn4, Mn5, Mn6) synthesized with TEG.

**Figure 10** shows the TG curves of the NPs, presenting the weight loss in correlation to the temperature (25-900 °C). For the  $\text{MnCO}_3$  NPs with the coating of TEG (Fig. 10A) a weight loss of 4% from 20 to 150 °C is obtained, due to water removal. As the heating continues, from 200 to 420 °C, a sharp weight loss of 34% is observed due to the decomposition of a quantity of the coating agent as well as the decomposition of manganese carbonate which gives off  $\text{CO}_2$  and forms manganese oxides. The cumulative organic content (% w/w) is 38%. Compared with the TGA curve of bulk  $\text{MnCO}_3$ , it can be concluded that most of the weight loss comes from the decomposition of carbonate ions and a small percentage comes from the presence of organic compounds on the surface of  $\text{MnCO}_3$  NPs. For the  $\text{MnOHCO}_3$  NPs with the TEG coating (Fig. 10B) an initial weight loss of 3% from 20 to 125 °C is observed, due to moisture in the sample. Then the removal of organics takes place in two steps, from 125 to 210 °C there is a weight loss of 5% and from 210 to 412 °C a sudden weight loss of 15% due to the decomposition of low molecular weight organic compounds, hydroxyls and the release of carbon dioxide.

The total weight loss of the NPs reaches 23% of its original mass. Lastly, for the  $\text{Mn}_2\text{O}_3/\text{MnO}_2$  NPs (Fig. 10C) the percentage of the moisture is 2%. From 100 to 440°C a sharp weight loss of 41% is observed due to the decomposition of TEG. The increase in mass, an exothermic effect, is due to the oxidation of  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  to  $\text{Mn}_3\text{O}_4$ . The cumulative organic content is 43%.



**Figure 10.** Thermogravimetric analysis (TGA) of Mn-based NPs (Mn4, Mn5, Mn6) synthesized with TEG.

The structural composition and crystallite size of all synthesized NPs using TEG as a polyol are presented in **Table 2**.

When employing  $\text{KMnO}_4$  as the manganese source in the presence of TEG the system is directed towards the synthesis of pure  $\text{MnCO}_3$  NPs. This outcome arises from a comprehensive redox reaction, where

manganese undergoes reduction from the +7 to +2. Concurrently, TEG undergoes complete oxidation, resulting in the formation of carbonate ions. Additionally, a small portion remains in lower oxidation products, such as ketones or aldehydes, serving as an organic coating on the surface of NPs.

In the case of the coordination Mn complex,  $\text{Mn}(\text{acac})_2$ , as a precursor and the use of an inorganic reducing agent, the synthesis of  $\text{MnCO}_3$  NPs with hydroxyls in the crystal lattice,  $\text{MnOHCO}_3$  NPs, takes place. This fact underscores that the utilization of NaOH induces the synthesis of  $\text{MnOHCO}_3$  NPs.

Finally, in the context of employing  $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  as the manganese source in conjunction with TEG, the synthesis yields manganese oxide NPs. Specifically, a mixture of trivalent and tetravalent manganese oxide NPs is generated. This outcome is attributed to the competitive interaction between nitrate ions, serving as oxidizing agents, and the polyol's reducing function. Consequently, the polyol undergoes incomplete oxidation, with  $\text{CO}_2$  not being fully produced as a result.

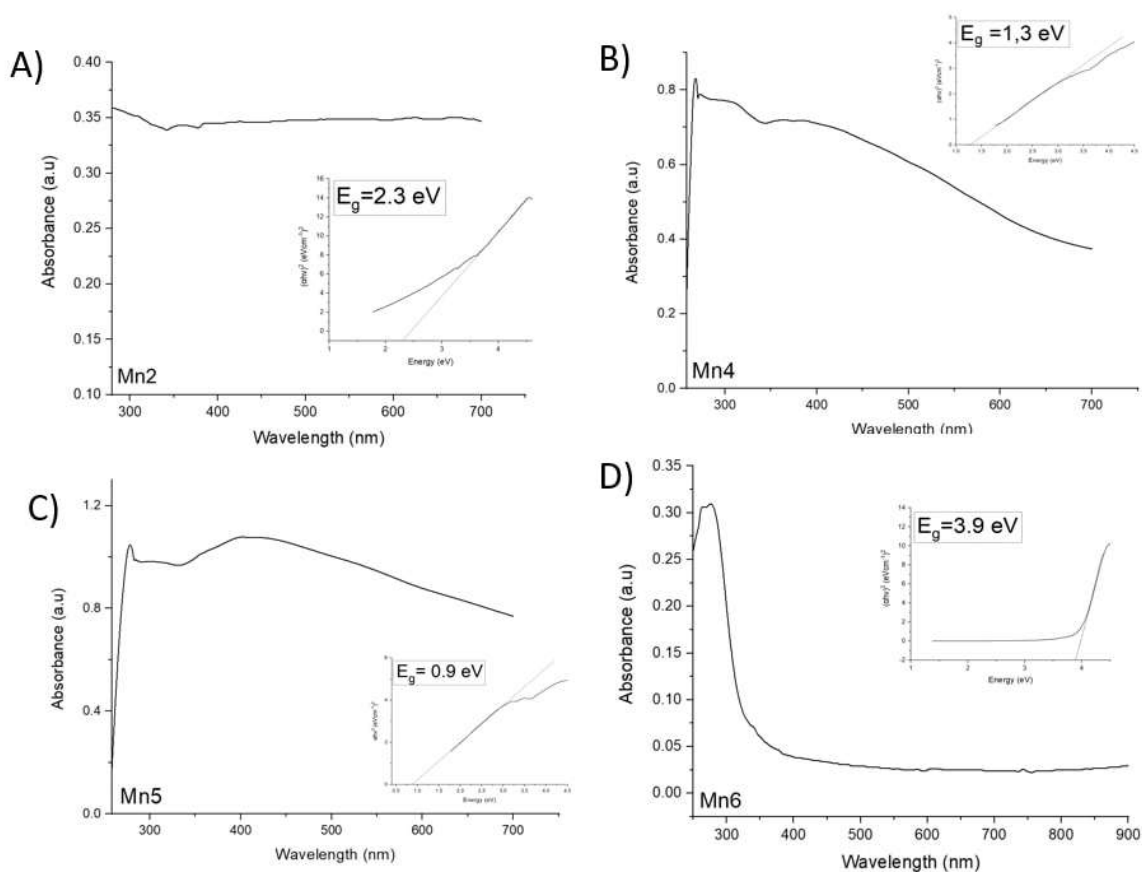
**Table 2. Characterization of synthesized Mn-Based NPs using TEG.**

Sample name	Precursor	Polyol	Reducing agent	Composition	dXRD (nm)	Org. coating (% w/w)	Carbonate ions (%w/w)
Mn4	$\text{KMnO}_4$	TEG	-	$\text{MnCO}_3$	25	2	32
Mn5	$\text{Mn}(\text{acac})_2$	TEG	NaOH	$\text{MnOHCO}_3$	41		
Mn6	$\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	TEG	-	$\text{Mn}_2\text{O}_3$ (92%) $\text{MnO}_2$ (8%)	140	41	-

The stabilization of synthesized Mn-based NPs was confirmed by measuring their average hydrodynamic particle size (Mean  $\pm$  PDI) and  $\zeta$ -potential. The average size of  $\text{MnCO}_3@\text{OAm}$  NPs is  $293 \pm 0.1$  nm, while the  $\zeta$ -potential was determined to be slightly positive  $+8.7 \pm 1$  mV. In contrast,  $\text{MnCO}_3@\text{TEG}$  NPs display a larger average size of  $920 \pm 0.213$  nm, accompanied by an average  $\zeta$ -potential of  $+9.7 \pm 1.1$  mV. The increased hydrodynamic size can be attributed to particle aggregation, as corroborated by TEM images showcasing peanut-shaped structures. The  $\text{MnOHCO}_3@\text{TEG}$  NPs have an average size of  $1.31 \pm 0.123$   $\mu\text{m}$ , with an average value of  $\zeta$ -potential  $+2.5 \pm 0.9$  mV, similarly indicating aggregation contributing to the larger hydrodynamic size. Finally,  $\text{Mn}_2\text{O}_3/\text{MnO}_2@\text{TEG}$  NPs possess an average size of  $322 \pm 0.29$  nm with a slightly negative value of  $\zeta$ -potential  $-4.6 \pm 1.3$  mV.

The UV-Vis absorption spectrum analysis of  $\text{MnCO}_3$  and  $\text{MnOHCO}_3$  NPs reveals a broad absorption range spanning from 200 to 900 nm<sup>43</sup>. Using Tauc's formula, the calculated band gaps for these NPs were found to be 2.3 eV for  $\text{MnCO}_3@\text{OAm}$  NPs, 1.3 eV for  $\text{MnCO}_3@\text{TEG}$  NPs, and 0.9 eV for

MnOHCO<sub>3</sub>@TEG NPs. This data underscores their suitability for semiconductive applications. In contrast, Mn<sub>2</sub>O<sub>3</sub>/MnO<sub>2</sub>@TEG NPs do not exhibit any UV-Vis absorption, and the band gap was determined to be 3.9 eV.



**Figure 11.** UV-Vis absorption spectrum of Mn-based NPs (Mn2, Mn4, Mn5, Mn6) in DMSO.

#### 4. Conclusions

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