Sonochemical-Assisted Coprecipitation Synthesis of Body-Centered Tetragonal Mn$_3$O$_4$ Spinel Nanostructures Using Polyethylene Glycol Template Agent

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Abstract The excellent characteristics of Mn$_3$O$_4$ nanomaterials have driven many experts to carry on exploring improved approaches for Mn$_3$O$_4$ fabrication. Herein, Mn$_3$O$_4$ nanostructures have been synthesized via sonochemical-assisted coprecipitation method. Polyethylene glycol (PEG-6000) with various concentrations was employed as a surface coating. The combination of coprecipitation and ultrasonication has led to the formation of Mn$_3$O$_4$ nanoparticles which were well-confirmed by three different characterization instruments, i.e., X-ray diffraction (XRD), scanning electron microscopy (SEM) along with energy dispersive X-ray (SEM-EDX), and Fourier transform infrared (FTIR). The XRD data collection and analysis reveal the presence of single-phase of Mn$_3$O$_4$ spinels. The Rietveld refinement dictates the establishment of tetragonal distortion along the c-axis creating a body-centered tetragonal spinel structure with a space group of I41/AMDS. In addition, the SEM-EDX and FTIR data support the experimental results obtained by XRD.

Keywords: Sonochemical-assisted coprecipitation, tetragonal spinel, nanostructures, Mn$_3$O$_4$

1. Introduction

Huge interest in the investigation of spinel oxide nanomaterials has been escalating in terms of both fundamental and technological features over the last decades attributable to the tunability of their remarkable properties [1–3]. One of the most outstanding spinel oxides goes to Mn$_3$O$_4$ nanomaterials, being recognized as their superior performances for green hi-tech applications, e.g., electrochemical supercapacitive electrode [3], organic pollutant degradation agent [4], photocatalyst [1], room temperature gas sensing [5], buffer layer in solar cell [6], temperature sensor in prosthetic glove [7], and water treatment [8]. The pursuit of finding the most effective approach has, therefore, become the scientific concern, particularly in the fields of nanoscience and nanotechnology.

To date, numerous methods have been established for the fabrication of Mn$_3$O$_4$ nanomaterials with particular shapes, and these we can quote: (1) coin-like structures and nanospheres of Mn$_3$O$_4$ were prepared using coprecipitation, hydrothermal, and sol-gel methods [9], (2) hexagonal nanoparticles and nanoplates of Mn$_3$O$_4$ were respectively fabricated by means of solvothermal
oxidation and solvent-assisted hydrothermal oxidation routes [10], (3) \( \text{Mn}_3\text{O}_4 \) nanoparticles were prepared via one pot and green methods using ethylene deep eutectic solvent [11], combination of coprecipitation and sonochemical method [12] and simple coprecipitation [13], (4) \( \text{Mn}_3\text{O}_4 \) nano-octahedra were prepared by ethylenediamine-mediation [14], (5) \( \text{Mn}_3\text{O}_4 \) nanotubes were shaped via \( \beta \)-\( \text{Mn}_2\text{O}_3 \) nanotubes reduction [15] and via galvanic replacement reaction [16], (6) \( \text{Mn}_3\text{O}_4 \) nanosheets were fabricated through stirring of ethanalamine, deionized water, and manganese chloride [17], and (7) \( \text{Mn}_3\text{O}_4 \) nano frames with hollow octahedra were synthesized by means of template-assisted hydrothermal route.

All of those reports have the same point of view that the crystal structure, shape, particle size, and monodispersity of hausmannite (\( \text{Mn}_3\text{O}_4 \)) nanomaterials determine their tailored performances. Consequently, a fabrication route to control the highly crystallized \( \text{Mn}_3\text{O}_4 \) is crucial [18]. Templates have been widely used to overcome the van der Waals contact between the nanoclusters leading to uncontrolled aggregation and to reduce the surface energy [19]. Among the frequently-used templates, PEG with ordered and uniform chain polymeric structures is claimed as a good template agent [11,19,20]. Simply put, the introduction of PEG as the template in metal oxides, including \( \text{Mn}_3\text{O}_4 \), takes a good control on the crystal growth kinetics [21].

In this present study, we report the successful synthesis of \( \text{Mn}_3\text{O}_4 \) with body-centered tetragonal spinel structure through sonochemical-assisted coprecipitation approach at room temperature under the incorporation of PEG template. \( \text{NH}_3\text{OH} \), an active precipitating agent, and acoustic cavitation during the synthesis process, in addition to the presence of PEG, play a decisive role in creating \( \text{Mn}_3\text{O}_4 \) with nanorods and nanospheres morphologies.

2. Methods
One gram of PEG-6000 and five grams of \( \text{MnCl}_2\cdot4\text{H}_2\text{O} \) were separately dissolved in 40 ml and in 5 ml water, respectively. The PEG solution was then added to the \( \text{MnCl}_2\cdot4\text{H}_2\text{O} \) solution with different concentrations, based on the volume ratio of PEG: \( \text{MnCl}_2\cdot4\text{H}_2\text{O} \), i.e., 1:1 (PEG #1), 1:2 (PEG #2), 1:3 (PEG #3), 1:4 (PEG #4), and 1:5 (PEG #5). \( \text{NH}_3\text{OH} \) was wisely dropped into the PEG- \( \text{MnCl}_2\cdot4\text{H}_2\text{O} \) solution while stirring at room temperature for 30 minutes and successively sonicated at 40 kHz for the other 30 minutes. The precipitate was immediately filtered and washed to reach neutral pH before drying in a furnace at 100 °C for 60 minutes. This reasonably simple and straightforward approach can produce \( \text{Mn}_3\text{O}_4 \) nanoparticles.

Characterization and analysis are essential parts of exploring the properties of the as-prepared sample. Therefore, a fixed divergence slit of XRD using Cu-Kα radiation was activated for crystallographic analysis. The XRD data was semiquantitatively analyzed by RIR approach and quantitatively evaluated by the Rietveld method. The morphology of \( \text{Mn}_3\text{O}_4 \) nanoparticles was visualized by SEM, as well as their elemental content by SEM-EDX. Furthermore, the functional groups within \( \text{Mn}_3\text{O}_4 \) were investigated using FTIR.

3. Results and Discussion
The identical XRD patterns of all prepared samples are depicted in Figure 1, including the details for the Bragg planes. The semi-quantitative analysis shows that only hausmannite phase, reference code of 01-080-0382, with spinel structure, does occur in the samples. The sample of the search-match analysis output is given in Figure 2. The previous work [12] concluded that the pH during the sonochemical-assisted coprecipitation process was crucial to obtain highly pure \( \text{Mn}_3\text{O}_4 \), and the single-phase \( \text{Mn}_3\text{O}_4 \) spinel structure was obtained at pH = 10. And yet, this current study, by the addition of PEG, opens up a new opportunity to successfully control the preparation of single-phase hausmannite \( \text{Mn}_3\text{O}_4 \) nanoparticles even the process was conducted at normal pH. The nano-sized behaviors of the \( \text{Mn}_3\text{O}_4 \) can be tracked from the shape of the XRD profiles and particle size calculation.
A careful Rietveld refinement, using Rietica program [22], yields the crystallographic features of the Mn$_3$O$_4$. The good of fitness values lies on the scale of 0.5 – 1.0%. These are below the minimum criteria, i.e., 4% [23], for the acceptable Rietveld refinement analysis. The lattice parameters and average particle size, derived from Rietica, can be seen in Table 1. As revealed in Figure 1 and Figure 2, Table 1 provides more information on the crystallographic data. The lattice parameters of the body-centered tetragonal Mn$_3$O$_4$ spinels are about 5.76 Å and 9.46 Å, respectively for $a = b$ and $c$ lattices. Those are in line with other reports [5,11,20]. Meanwhile, the average crystal sizes are in between 38-42 nm. It implies that the introduction of PEG template on the Mn$_3$O$_4$ fabrication plays a decisive role in controlling the good quality of Mn$_3$O$_4$ nanoparticles.
Table 1. Lattice parameter and average crystal size of spinel Mn$_3$O$_4$ nanoparticles.

| Mn$_3$O$_4$ with | Lattice parameter (Å) | Average crystal size (nm) |
|-----------------|-----------------------|---------------------------|
|                 | $a = b$               | $c$                       |                             |
| PEG #1          | 5.7598(6)             | 9.45830(10)               | 38.01(13)                  |
| PEG #2          | 5.7624(9)             | 9.4610(11)                | 41.65(12)                  |
| PEG #3          | 5.7619(9)             | 9.4583(14)                | 39.06(10)                  |
| PEG #4          | 5.7627(8)             | 9.4610(12)                | 48.69(12)                  |
| PEG #5          | 5.76523(8)            | 9.4677(11)                | 41.67(11)                  |

Figure 3. SEM images of spinel Mn$_3$O$_4$ nanostructures produced by sonochemical-assisted coprecipitation method using PEG template.

Figure 4. SEM-EDX profile of spinel Mn$_3$O$_4$ nanoparticles with PEG #4.
The tetragonal distortion originates the tetragonal spinel structure of the Mn$_3$O$_4$ due to the active Jahn-Teller effect [24]. It drives the Mn$^{3+}$ ions to be unstable in octahedral sites establishing a close-packed arrangement, and the Mn$^{2+}$ ions are likely to occupy the tetrahedral sites. The Mn$^{3+}$ ions as the central ions in the octahedral sites provide the presence of a weak field. It is because the Mn$^{3+}$ ions exhibit $t_{2g}^3 e_g^1$ configuration, rather than $t_{2g}^4 e_g^0$. This configuration results in a tetragonal distortion along the c-axis. Therefore, the Mn$_3$O$_4$ crystalizes in a body-centered tetragonal spinel nanostructure. The distribution of Mn$^{2+}$ ions over octahedral and tetrahedral sites cannot be described by classical elastic and electrostatic energies viewpoint. Unlike other cations with a “noble gas” outer electron shell configuration, Mn$^{2+}$ ions with a half-full d-shell are more compressible in such a way that they are easier to occupy the tetrahedral sites [25]. The deeper look into the lattice parameter values reveals that the $a$ and $c$ value are relatively smaller than that of the Mn$_3$O$_4$ single crystal. It takes place because the cation vacancies occur in the octahedral sites transforming three Mn$^{3+}$ ions into Mn$^{4+}$ ions that do not give any contribution to the Jahn-Teller effect. Also, there exists positive valence states enhancement in the octahedral sites [24–26].

The morphologies of the as-prepared Mn$_3$O$_4$ are shown in Figure 3. The SEM images capture nanospheres and nanorods morphologies of the Mn$_3$O$_4$. The diameters for the sphere-shaped and rod-shaped Mn$_3$O$_4$ nanostructures are ranging from 10 to 40 nm, and these average diameters meet the value obtained by the XRD data analysis. Furthermore, the SEM-EDX test (as displayed in Figure 4) demonstrates the only presence of mangan and oxygen atoms with an atomic ratio of mangan-to-oxygen is nearly 0.7 with which exhibit tolerable value compared with the empirical ratio of mangan-to-oxygen in the Mn$_3$O$_4$ compound [27,28]. In comparison, the results are in a good agreement with Mn$_3$O$_4$ nanosphere and nanorods produced by the same template but more complex synthesis process [11].

The infrared transmittance bands of the Mn$_3$O$_4$ nanostructures are drawn in Figure 5. Strong infrared absorption near 500 cm$^{-1}$ and 600 cm$^{-1}$ correspond to the Mn–O stretching on both tetrahedral and octahedral sites [29]. It supports the XRD and SEM-EDX findings on the formation of body-centered tetragonal spinel of Mn$_3$O$_4$. –OH bending in the forms of γ–OH, δ–1–OH, and δ–2–OH is identified at the wavenumber of around 1100 cm$^{-1}$ [30]. The water molecule absorption in the Mn$_3$O$_4$ is detected by the broad infrared absorption at 3350 cm$^{-1}$ and 2100 cm$^{-1}$, also O–H strain at 1600 cm$^{-1}$ [30]. The C–H and C–O functional groups are respectively shifted to 1095 cm$^{-1}$ and 955 cm$^{-1}$, nearly 50 cm$^{-1}$ smaller than those in the pure PEG [19]. Since the template molecules in the adsorbed region are influenced by the solid-state surface field, the presence of the C–H functional group at the lower region reflects the strong hint that PEG is on the surface of Mn$_3$O$_4$ nanostructures [31].

![Figure 5](https://example.com/figure5.png)  
Figure 5. Infrared transmittance characteristics of spinel Mn$_3$O$_4$ nanoparticles.
4. Conclusion

A room temperature sonochemical-coprecipitation approach to synthesis Mn$_3$O$_4$ nanostructures has been successfully conducted by the incorporation of PEG as the templating agent. The crystal structure of the produced Mn$_3$O$_4$ is body-centered tetragonal spinel having $a = b$ and $c$ crystal lattices of about 5.76 Å and 9.46 Å, respectively. Any impurities are not detected in all samples, implying that the use of PEG is useful to prepare single-phase Mn$_3$O$_4$ with the shapes of nanospheres and nanorods. The SEM-EDX confirms the XRD data collection and analysis. The presence of PEG polymeric chain on the MN$_3$O$_4$ surface is traced by the FTIR spectra.

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References

[1] Sheikhshoae I, Ramezanpour S and Khatamian M 2017 Synthesis and characterization of thallium doped Mn$_3$O$_4$ as superior sunlight photocatalysts J. Mol. Liq. 238 248–53
[2] Rizzuti A, Dassisti M, Mastrorilli P, Sportelli M C, Cioffi N, Picca R A, Agostinelli E, Varvaro G and Caliandro R 2015 Shape-control by microwave-assisted hydrothermal method for the synthesis of magnetite nanoparticles using organic additives J. Nanoparticle Res. 17 408
[3] Nwankwo M C, Nwanya A C, Agbugu A, Ekwealor A B C, Ejikeme P M, Bucher R, Osuji R U, Maaza M and Ezema F I 2018 Electrochemical supercapacitive properties of SILAR-Deposited Mn$_3$O$_4$ electrodes Vacuum 158 206–14
[4] Ma Q, Zhang X, Guo R, Zhang H, Cheng Q, Xie M and Cheng X 2019 Persulfate activation by magnetic γ-Fe$_2$O$_3$/ Mn$_3$O$_4$ nanocomposites for degradation of organic pollutants Sep. Purif. Technol. 210 335–42
[5] John N, Thomas P, Divya K V and Abraham K E 2018 Enhanced room temperature gas sensing of aligned Mn$_3$O$_4$ nanorod assemblies functionalized by aluminum anodic membranes Nanotechnology 29 335503
[6] Lee C-H, Lee S, Yeo J-S, Kang G-S, Noh Y-J, Park S-M, Lee D C, Na S-I and Joh H-I 2018 Hybrid materials of upcycled Mn$_3$O$_4$ and reduced graphene oxide for a buffer layer in organic solar cells J. Ind. Eng. Chem. 61 106–11
[7] Kumar A, Singla M L, Kumar A and Rajput J K 2019 Fabrication and linearisation of conformable POMANI-Mn$_3$O$_4$ nanocomposite based thermistor for temperature monitoring applications in prosthetic gloves Sens. Actuators Phys. 285 588–98
[8] Park J-H, Jang I, Kang Y, Kim Y C and Oh S-G 2014 Morphology-controlled synthesis of polystyrene-Mn$_3$O$_4$ nanocomposites using surfactant and their application for water treatment Colloids Surf. Physicochem. Eng. Asp. 441 340–5
[9] Rani B J, Ravina M, Ravi G, Ravichandran S, Ganesh V and Yuvakkumar R 2018 Synthesis and characterization of hausmannite (Mn$_3$O$_4$) nanostructures Surf. Interfaces 11 28–36
[10] Ahmed K A M, Zeng Q, Wu K and Huang K 2010 Mn$_3$O$_4$ nanoparticles and nanofibers: Synthesis, characterization, electrochemical and catalytic properties J. Solid State Chem. 183 744–51
[11] Karimi M and Eshraghi M J 2017 One-pot and green synthesis of Mn$_3$O$_4$ nanoparticles using an all-in-one system (solvent, reactant and template) based on ethaline deep eutectic solvent J. Alloys Compd. 696 171–6
[12] Hidayat N, Taufiq A, Sunaryono S, Hidayat S, Heriyanto H and Prayekti E B 2018 Combination of coprecipitation and sonochemical methods in synthesizing spinel hausmannite nanomaterial J. Penelit. Fis. Dan Apl. JPFA 8 1–9
[13] Taufiq A, Muzammil M, Fuad A, Hidayat N, Sunaryono S, Mufti N, Hidayat A, Diantoro M and Munasir M 2018 Preparation, structural and dielectric behaviors of Co$_x$Mn$_{1-x}$Mn$_3$O$_4$ (0 ≤ x ≤ 1) nanoparticles IOP Conf. Ser. Mater. Sci. Eng. 367 012050
[14] Guo C X, Chen S and Lu X 2014 Ethylenediamine-mediated synthesis of Mn$_3$O$_4$ nano-octahedrons and their performance as electrocatalysts for the oxygen evolution reaction Nanoscale 6 10896–901

[15] Bai Z, Fan N, Ju Z, Guo C, Qian Y, Tang B and Xiong S 2013 Facile synthesis of mesoporous Mn$_3$O$_4$ nanotubes and their excellent performance for lithium-ion batteries J. Mater. Chem. A 1 10985–90

[16] Dong H, Koh E K and Lee S-Y 2009 Synthesis of Ag-Mn$_3$O$_4$ core-shell nanorods and Mn$_3$O$_4$ nanotubes from sacrificial Ag nanorod templates J Nanosci Nanotechnol. 9(11):6511-7

[17] Zhen M, Zhang Z, Ren Q and Liu L 2016 Room-temperature synthesis of ultrathin Mn$_3$O$_4$ nanosheets as anode materials for lithium-ion batteries Mater. Lett. 177 21–4

[18] Jothi P R, Pramanik M, Li C, Kannan S, Malgras V, Salunkhe R R and Yamauchi Y 2016 Controlled synthesis of highly crystallized mesoporous Mn$_2$O$_3$ and Mn$_3$O$_4$ by using anionic surfactants Chem. – Asian J. 11 667–73

[19] Karaoğlu E, Deliçöz H, Sözeri H, Baykal A and Toprak M S 2011 Hydrothermal synthesis and characterization of PEG- Mn$_3$O$_4$ nanocomposite Nano-Micro Lett. 3 25–33

[20] Hill R J and Howard C J 1987 Quantitative phase analysis from neutron powder diffraction data using the Rietveld method J. Appl. Crystallogr. 20 467–74

[21] Durmus Z, Kavas H, Baykal A and Toprak M 2009 A green chemical route for the synthesis of Mn$_3$O$_4$ nanoparticles Open Chem. 7 555–559

[22] Baykal A, Köseoğlu Y and Şenel M 2007 Low temperature synthesis and characterization of Mn$_3$O$_4$ nanoparticles Open Chem. 5 169–176

[23] Göüzük F, Köseoğlu Y, Baykal A and Kavas H 2009 Synthesis and characterization of Co,Zn$_{1-x}$Fe$_2$O$_4$ magnetic nanoparticles via a PEG-assisted route J. Magn. Magn. Mater. 321 2170–7