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Hydrothermally Derived $MnCo_2O_4$ Spinel Material for Energy Storage Applications: A Physicochemical Study

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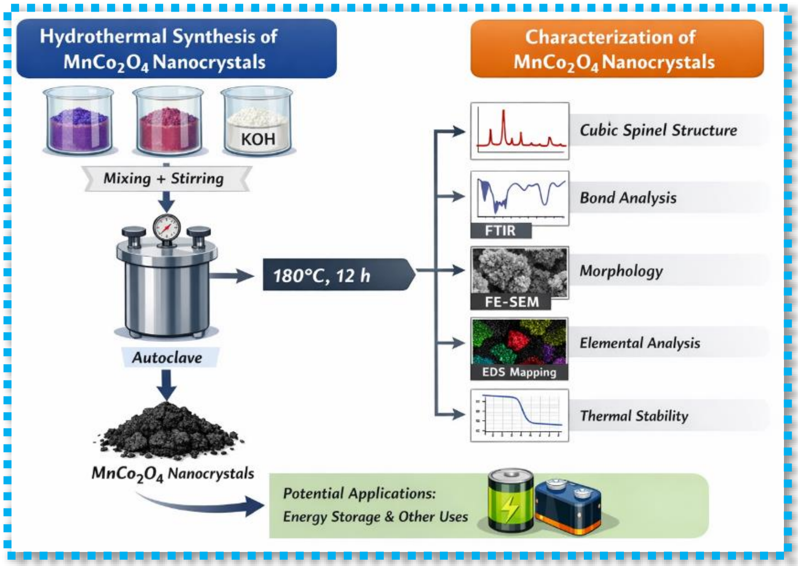
ABSTRACT: In this research, we reported a facile hydrothermal technique for the preparation of $MnCo_2O_4$ nanocrystalline material using KOH. The physico-chemical properties of $MnCo_2O_4$ material were examined by thermogravimetric analysis, Powder X-ray analysis, FTIR studies, microscopy analysis, and ED-spectroscopy with quantitative mapping. The X-ray diffraction and FTIR studies of $MnCo_2O_4$ material confirm a cubic spinel structure with an Fd3m space group and an average crystalline size of 45 nm from the Scherrer formula. Low-frequency FTIR analysis has also confirmed where the ions are in the spinel structure of $MnCo_2O_4$ material. Micrographs show uneven $MnCo_2O_4$ agglomerations. EDS examination and elemental mapping confirmed the presence of Mn, Co, and O. The co-precipitated material may be useful for energy storage and other applications.

Keywords: $MnCo_2O_4$ Material; Thermal analysis; Hydrothermal process; X-ray diffraction; Structural properties.

GRAPHICAL ABSTRSCT



1. INTRODUCTION

Over the past decades, the concentration of materials with a spinel structure has gained much attention, which possesses physicochemical characteristics. Spinel compounds such as $ZnFe_2O_4$, $MnFe_2O_4$, $MgFe_2O_4$, $CoMn_2O_4$, Mn_3O_4 and Co_3O_4 show evidence of physicochemical behavior and being studied for creating and developing potential applications in the field of memory devices, semiconductor modules, gas sensors, memory shield, spintronics, supercapacitors and so on [1, 2]. $MnCo_2O_4$ is a potentially important Pb-free material that exhibits physico-chemical properties and has received great attention in several applications like a supercapacitor, transportation, telecommunication, medical, and energy) due to their elemental abundance and cost-effective [3].

For materials like manganese cobalt oxide, many cation distributions have been proposed in the literature survey including $Co^{2+}[Co^{2+}Mn^{4+}]O_4$, Co^{3+} $[Mn^{2+}Co^{3+}]O_4$, Co^{2+} $[Mn_{0.35}{}^{2+}Co^{3+}Mn_{0.29}{}^{3+}Mn_{0.36}{}^{4+}]O_4$. Based on these findings, it is possible to conclude that these material preparation conditions have a potential impact on physicochemical properties such as phase, morphology, cation distribution, and vibrational [4].

Many researchers are being forced to try to produce metal oxide compounds. Among them, the most common methods for producing manganese cobalt oxide material include sol-gel, co-precipitation, combustion approach, ball milling technique, mechanochemical method, and wet chemical, etc., However, some of these strategies are often costly, time-consuming, unreliable, and difficult to use on a broad scale. As a result, we explored hydrothermal synthesis, in which one can precisely regulate the hydrolysis, nucleation, and development of crystalline materials by varying the reaction heat and pressure. It is worth investigating the effect of this synthesis on the physicochemical parameters of manganese cobalt oxide [5].

In this work, we examine a facile hydrothermal process to obtain manganese cobalt oxide material using potassium hydroxide. The physico-chemical of the synthesized manganese cobalt oxide material was functionally studied by various analysis techniques like power X-ray measurement, FTIR analysis, Morphology studies, ED-spectrometry, and quantitative mapping analysis. The characterized results are interpreted in terms of the structural and morphological behavior of the manganese cobalt oxide material.

2. EXPERIMENTAL

2.1. Materials

Manganese chloride, potassium hydroxide, and cobalt (II) chloride were all acquired from Sigma Aldrich. For the synthesis technique, deionized water was used along with all of the reagents, which were not further purified.

2.2. Synthesis

A facile hydrothermal process was used to synthesize manganese cobalt oxide material. A weighing machine was used to weigh each product. Then, while stirring with a magnetic stirrer at 660 rpm, 20 ml of distilled H_2O was progressively mixed to make the solution. The final component is KOH, which will be gradually added to the mixture. This will change the color of the combination to shift from red to greenish blue. The material was then placed in a Teflon chamber, followed by a stainless-steel chamber that was tightly sealed with covers and held at 200 degrees Celsius for 12 hours in the Oven. After the hydrothermal, the manganese cobalt oxide material was carefully separated and produced in a suspension by being washed repeatedly with distilled water and methanol. The sample is dried for 12 hours at 80 C in a vacuum oven and stored for further studies.

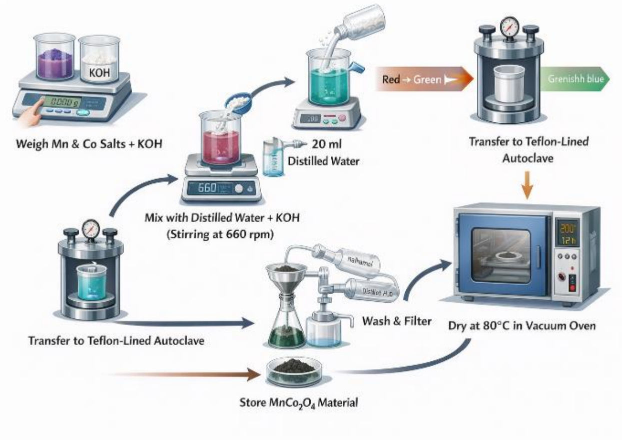


Fig. 2 Synthesis schematic of the $MnCo_2O_4$ prepared via hydrothermal process.

2.3. Materials characterization

PerkinElmer Simultaneous Thermal Analyzer, TGA analysis was performed using an N_2 environment. The phase identification was performed by Panalytical-Empyrean X-ray diffractometer, with wavelength, $\lambda = 1.54$ Å at 45 kV over 10 to 80°. The phase was identified using conventional patterns from the International Centre for Diffraction Data (ICDD) database. Spectra were acquired using a Nicolet, Thermo Electron FTIR spectrometer (USA) within a range of 400-4000 cm^{-1} (mid-IR region). The sample's microstructure was looked at with a 20 keV JEOL SEM (Instrument: JSM-6010LA) scanning electron microscope (SEM). Secondary electron imaging was used to take the SEM pictures (SEI). Using double-sided carbon tape, the sample was stuck to the brass stub. Fields of the sample were put in a high-vacuum instrument and InTouchScope JSM software was used to make micrographs of the sample.

3. RESULTS AND DISCUSSION

3.1. Thermal analysis

Fig. 2 TGA curve of the manganese cobalt oxide generated via hydrothermal process. As shown in Fig. 1 a steep weight loss occurs in $MnCo_2O_4$ at 350C, due to the emission of CO_2 molecules from the decomposition of the precursor.

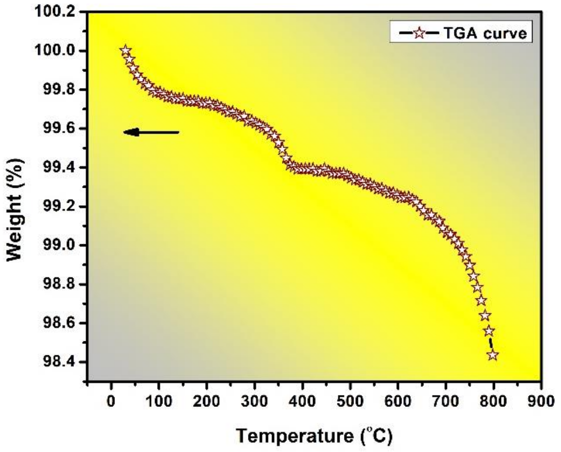


Fig. 2 TGA curve of the $MnCo_2O_4$ generated via hydrothermal process.

After 350C, gradually started to decrease ie. No significant weight loss was detected in the TGA graph. Hence, it proposes that synthesized materials are highly crystalline in nature [6].

3.2. XRD investigation

To explore the phase evolution of manganese cobalt oxide using the hydrothermal process, structural XRD studies were utilized. Fig. 3 shows the room-temperature XRD pattern of manganese cobalt oxide. The 2 angles, which are indexed to crystal planes are related to an FCC spinel (card:023-1237) which has the chemical formula of $MnCo_2O_4$ with Fd3m space group [7]). All the XRD peaks of the samples displayed strong and distinct peaks, which is evidence that the materials have a good crystalline nature. The peak broadening in the XRD pattern is another indication that the sample has become increasingly surface-rich concerning their volume. Within the bounds of the XRD's range, we were unable to identify any further phases. This justifies the finding that the XRD investigation revealed a single phase.

The typical average grain sizes, D_{avg} was calculated from Scherrer formula [8],

$$D_{avg} = 0.9\lambda/\beta\cos\theta \qquad (1)$$

Where λ denotes the X-ray wavelength (Å), D_{avg} implies the average grain size, β implies the full width at half maximum, and θ implies the Bragg's angle. The manganese cobalt oxide material had a D_{avg} value of 45 nm. When compared to the value obtained using other techniques for the manufacture of manganese cobalt oxide material [8], this value is favorable.

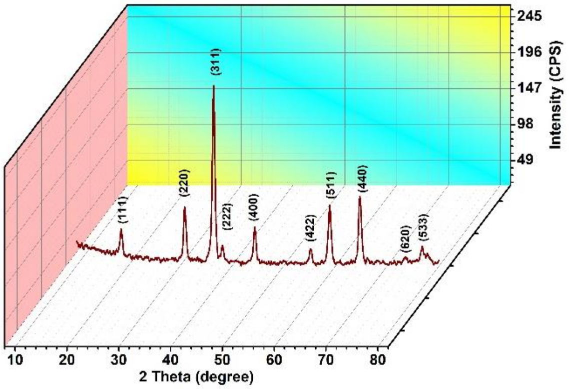


Fig. 3 XRD pattern of the MnCo$_2$O$_4$ generated via hydrothermal process.

3.3. FTIR studies

The FTIR spectra of the manganese cobalt oxide nanocrystalline material collected over the wavelength range 400-4000 cm^{-1} are displayed in Fig. 4. In most cases, the bands that are the most intense can be found in the range of 700–350 cm^{-1}, and both the wave number and the strength of these bands are determined by the cation distribution and occupancy of the cations in spinel-type sublattices. In the case of MnCo$_2$O$_4$, the band that appears at the lower wave number (ε_1) at 541 cm^{-1} is recognized as the octahedral complexes, whilst the band that appears at the higher wave number (ε_2) at 664 cm^{-1} is recognized to the tetrahedral developments [9-11]. In the MnCo$_2$O$_4$ nanocrystalline material, the FTIR analyses provided additional confirmation of the locations of the ions within the spinel structure.

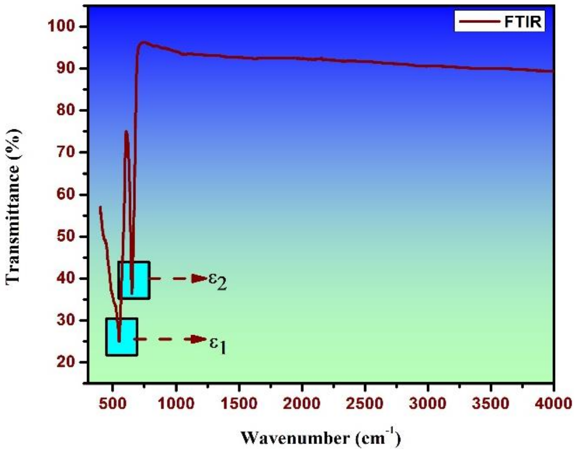


Fig. 4. FTIR pattern for the synthesized manganese cobalt oxide generated via hydrothermal process.

3.4. Microscopic analysis

The SEM micrographs of the synthesized manganese cobalt oxide material are displayed in Fig. 5. The sample possessed an irregular structure and was observed to be comprised of agglomerated nanoparticles. It displayed dissimilar sizes (10-100 nm) [12-15]. This may be attributed to the magnetic interaction between the particles during hydrothermal synthesis.

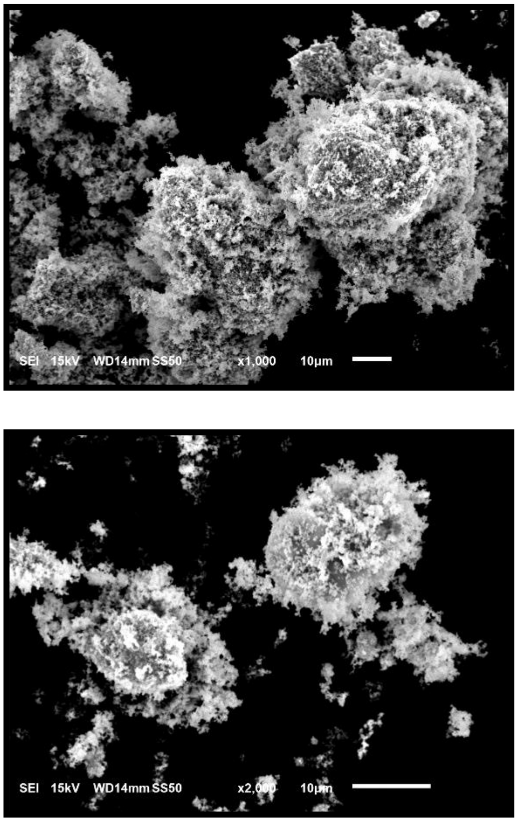


Fig. 5. SEM micrographs with 10 μm of the synthesized manganese cobalt oxide generated via hydrothermal process.

3.5. Energy Dispersive X-Ray, EDS analysis

Fig. 6 displays the elemental analysis of the manganese cobalt oxide produced by a hydrothermal technique. EDS spectra reveal the presence of the elements Mn, Co, and O. Within the limitations of our detector, no more elements were found. This represents the purity of the sample [16].

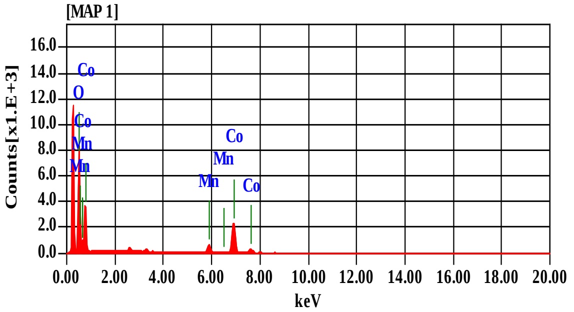
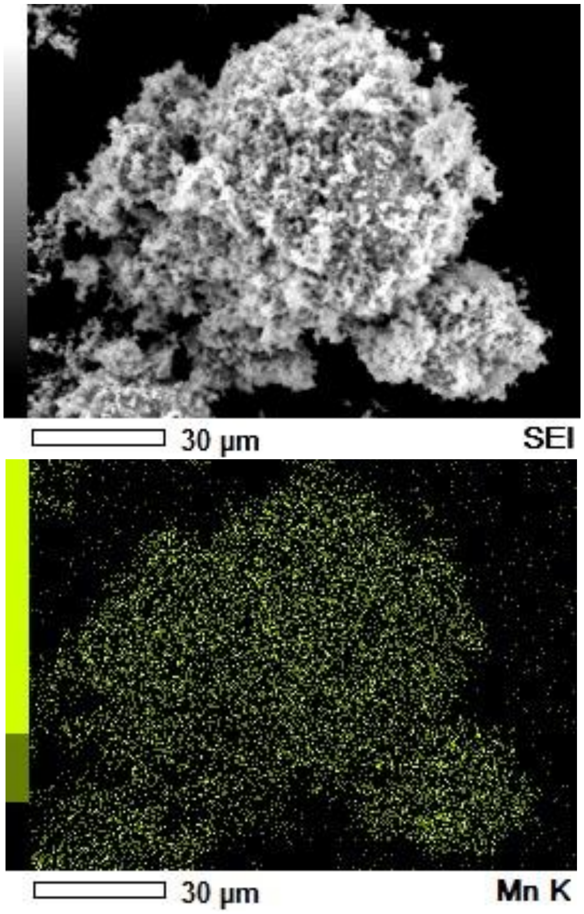


Fig. 6. EDS spectrum of the manganese cobalt oxide generated via hydrothermal process.

3.6. Elemental mapping analysis

Fig. 7 displays the quantitative mapping analysis of Mn, Co and O within the manganese cobalt oxide produced by a hydrothermal technique. The constituent cations are uniformly distributed throughout the sample.



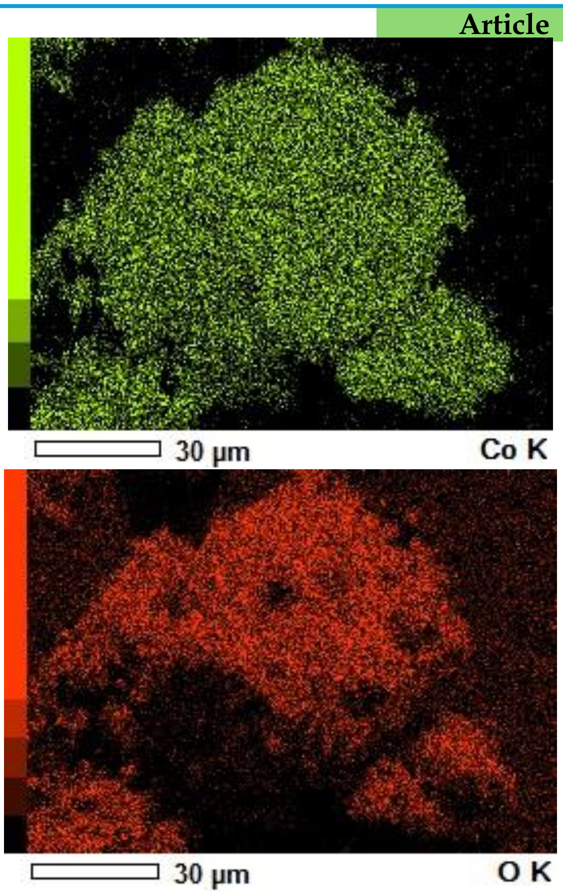


Fig. 7. Elemental mapping of the manganese cobalt oxide generated via hydrothermal process.

4. CONCLUSION

In conclusion, the $MnCo_2O_4$ nanocrystalline material was successfully obtained from facile hydrothermal process using KOH. The formation of the cubic spinel structure with an Fd3m space group and an average crystalline size of 45 nm was proved by XRD and FTIR analysis. Morphology studies reveal the formation of $MnCo_2O_4$ nanostructure with agglomerated particles. EDS examination and elemental mapping checked the existence of Mn, Co, and O in $MnCo_2O_4$ material. Hydrothermally synthesized material may be useful for energy storage and other applications.

Author contributions

Tholkappiyan Ramachandran: Writing-original draft, Conceptualization, Writing-review and editing, Methodology, Investigation; **Ramesh Kumar Raji:** Writing-review and editing, Formal analysis, Methodology.

Conflicts of interest

There are no conflicts to declare.

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