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Synthesis of Binary Manganese Cobalt Oxide ($MnCo_2O_4$) Nanomaterial in Environmentally Benign Aqueous Media

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Abstract: A new green synthetic approach of binary manganese cobalt oxide ($MnCo_2O_4$) nanomaterial with citric acid as a surfactant using the sol-gel method is investigated. In this process, water is considered a core solvent, and the synthetic approach is environmentally advantageous because of its low cost, easy preparation, and industrial viability due to this solvent. The determination of nanomaterial has been done by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and Fourier transform Infrared spectroscopy (FTIR). Highly dispersed characterization results are shown by synthesized nanomaterial. This green methodology proves an effective, eco-friendly, simple, and valuable approach for synthesizing $MnCo_2O_4$ nanomaterial.

Keywords: binary manganese cobalt oxide; sol-gel method; nanomaterial; microbial activity.

1. Introduction

General formula AB_2O_4 of Spinel structures are renowned materials in the catalysis field. Developing new nonmaterial for green energy applications has attracted the attention of researchers because of worsening global warming and energy scarcity problems [1,2]. Most energy consumed is extracted from fossil fuels, such as oil and natural gas. The strong global demand for energy is increasing rapidly and will be doubled in the next 15 years. This demand will probably cause a harmful disappearance of natural reserves and increase the pollution effect in the atmosphere [3,4]. Some transition metal oxides show excellent stability, high activity, low overpotential, and significant roundtrip efficiency associated with their possible oxidation states, off-stoichiometric compositions, defects, and vacancies [5-7].

Among the transition metal oxides, spinel $MnCo_2O_4$ (MCO) has been utilized for energy applications because it possesses certain unique properties, such as magnetic hysteresis behavior [1,8-11] and protective coating application [12]. Manganese cobalt oxide (MCO) can be synthesized using various procedures such as the Pechini method, sol-gel method, a co-precipitation method, microwave plasma preparation, and the oxide powders milling and spray pyrolysis [12,13].

In the present work, we have synthesized a spinel structure that consists of Mn(II) and Co(II) combined in the formula $MnCo_2O_4$, where Mn(II) occupies tetrahedral and Co(II) octahedral sites of crystal Structure using the facile Sol-gel method. Spinel structures embodied with 3d elements like Mn and Co, or Fe, Cr, and Ni, have high spin electron configurations due to oxygen ions being a weak field ligand. A great potential of $MnCo_2O_4$ as an electro-catalysis [6] and in polymer degradation [14] was reported.

To prepare an excellent material with all good and desirable physicochemical characteristics, the method of synthesis is very important. Numerous papers have been reported related to the synthesis methods of different spinel nanostructures. Some of the methods reported for electrochemical purposes are co-precipitation [13,15], sol-gel method [16], micro-emulsion method [17], and hydrothermal method [18]. For the Mn-Co spinel structure, the most implemented methods are precipitation [18,19], sol-gel method [16], hydrothermal method [19-23], combustion synthesis [1], or impregnation reaction [24]. In all these reported methods, water was used as the most important solvent, and citric acid was used as a surfactant in our work.

Herein, we synthesized a manganese-cobalt oxide ($MnCo_2O_4$) nanomaterial system in the presence of Citric acid by sol-gel method in an aqueous medium. This method has new characteristics of notable attention due to its low cost, easy preparation, and industrial capability. Synthesis of binary manganese-cobalt oxide nanomaterial by sol-gel technique is done using manganese chloride and cobalt chloride precursor and dried at 500°C. The structure and morphology of manganese-cobalt oxide nanomaterial have been studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), and energy-dispersive X-ray spectroscopy (EDX) respectively. The manganese cobalt nanomaterial synthesis has been performed using distilled water as the most important solvent.

2. Materials and Methods

2.1. Materials.

The chemicals were analytical grade and purchased from SD Fine Chemicals, Mumbai. These chemicals were used without further purification. All the aqueous solutions were prepared in distilled water.

2.2. Characterization methods.

The XRD pattern of manganese-cobalt oxide nanomaterial was recorded using a Rigaku X-ray Diffractometer with Cu K-α radiation source (λ=1.5406 A°) operated at 40 kV. Mn-CoO nanomaterial's structural morphology was studied using Field Emission Scanning Electron Microscope (FESEM) JEOL 6390LA, Japan, while Transmission Electron Microscopy (TEM). EDX analysis was performed using JEOL/JEM 2100, Japan, with an acceleration voltage of 200 kV. FTIR spectra of Mn-CoO nanomaterial were obtained by Shimadzu IR spectrophotometer.

2.3. Synthesis of $MnCo_2O_4$ oxide nanoparticles.

Synthesis of $MnCo_2O_4$ spinel oxide nanoparticles was carried out by the sol-gel method. Initially, 0.25 M of Manganese chloride and 0.25 M of cobalt chloride were dissolved separately in 50 ml of water. 0.1 N hydrochloric acid has improved the solubility of Manganese chloride and cobalt chloride in water. Both these solutions were mixed with constant stirring.

After mixing the solution, 1 gm of Citric acid solution was added as a surfactant. The pH of the above solution was adjusted at 8-8.5 (basic) using an NH_4OH solution. Precipitation was formed and stirred constantly for an hour at room temperature. The mixture was filtered using Whatman filter paper No. 42 and washed with deionized water 2-3 times. The obtained solid product was dried in an oven at around 100˚C for 2 hours. Finally, the dried material was calcinated for 3 hours at 500˚C in the furnace.

3. Results and Discussion

3.1. FTIR analysis of $MnCo_2O_4$ oxide nanomaterial.

FTIR absorption spectra of $MnCo_2O_4$ nanomaterial are shown in Figure 1. The peak at 3323.35 cm^{-1} showed O–H stretching vibrations of adsorbed H_2O molecules on the nanomaterial's surface. The absorption bands detected at 659.66 and 555.50 cm^{-1} are related to stretching vibrations of Mn–O and Co–O, respectively [18,25]. The absorption band at 1514 cm^{-1} is shown to surface adsorbed carbon dioxide. The stretching vibrations observed in the FTIR spectra are characteristic of metal oxides in spinel.

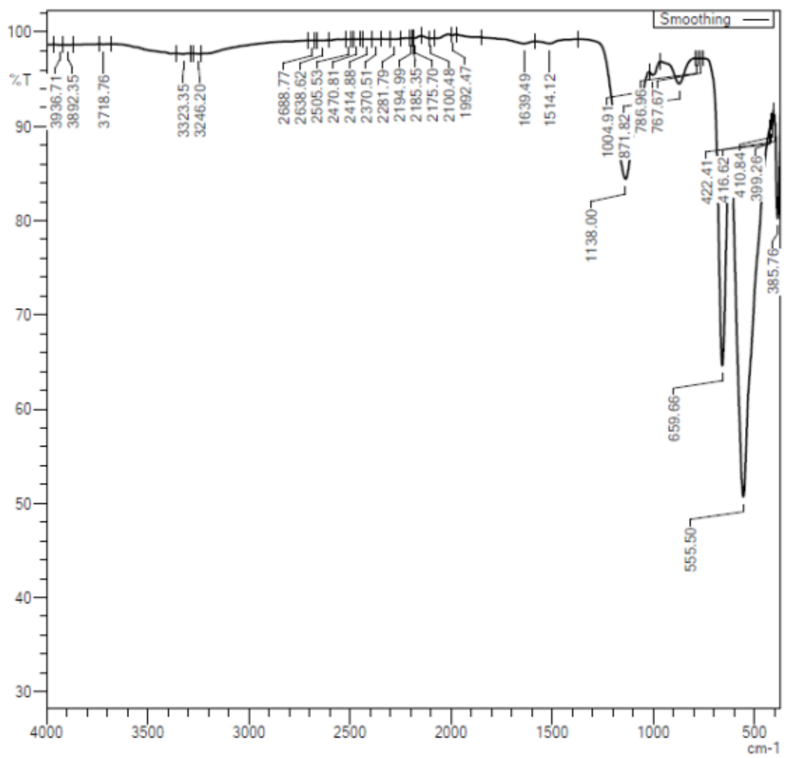

Figure 1. FTIR spectrum of $MnCO_2O_4$ nanoparticles in the spectrum range from 400 to 4000 cm^{-1}.

3.2. XRD characterization of $MnCo_2O_4$ oxide nanomaterial.

The XRD technique characterized the chemical, structural, and spectroscopic properties of MnCo2O4 nanomaterial. All the X-ray diffraction peaks can be indexed according to the standard data for $MnCo_2O_4$ (JCPDS card no. 23-1237), which is considered as mixed-valent oxides that acquire spinel structures in which the Mn and Co ions are distributed over tetrahedral (A) and octahedral (B) sites.

The results observed were found to be similar to results previously reported [26-28]. The diffraction peaks corresponding to the Miller indices of the material (Fig. 2) recognized intense lines at 2θ of 20.200 (111), 31.160 (220), 36.720 (311), 44.720 (400), 55.440 (422), 59.26 (511), 65.020 (440), 77.200 (533). The crystallite size of the sample was estimated by using Debye-Scherer's equation,

$$D= (0.9\ \lambda)/\beta\ (\cos\theta)$$

by measuring the line broadening of the main intensity peak, where λ is the wavelength of Cu Kα radiation, β is the full width at half-maximum, and θ is the Bragg's angle. The results (Figure 2) indicated that the average crystallite size of Mn-Co Oxide nanomaterial is 14.17 nm.

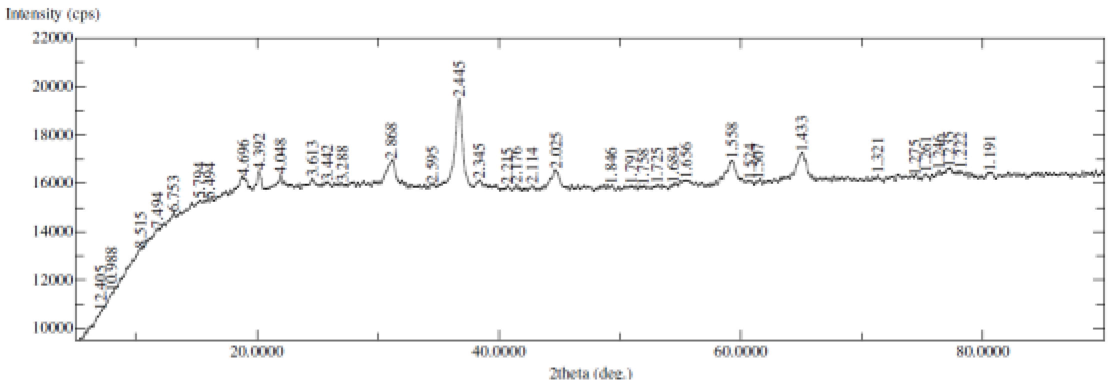

Figure 2. XRD pattern of $MnCo_2O_4$ oxide nanomaterial synthesized by sol-gel technique.

3.3. SEM, TEM & EDX studies of $MnCo_2O_4$ oxide nanomaterial.

The morphology and the complete structures of $MnCo_2O_4$ nanomaterial were contributed by scanning electron microscope (SEM) and energy-dispersive X-ray (EDX) spectroscopy. SEM images of $MnCo_2O_4$ nanomaterial synthesized by sol-gel method from chloride precursors strengthening the precursors at 500°C are shown in Figure 3.

The presence of Mn and Co and the Mn/Co ratio were determined by EDX analysis, which agrees perfectly with $MnCo_2O_4$ (Figure 4). This confirms the availability of manganese, cobalt, and oxygen with a weight percentage of 7.67%, 63.77%, and 25.77%, with atomic percentages of 4.78%, 37.04%, and 55.18%, respectively.

Transmission electron microscopy (TEM) image of $MnCo_2O_4$ nanomaterial synthesized by sol-gel method from chloride precursor showed the $MnCo_2O_4$ nanomaterial has spherical shaped nanomaterial with average material size between 19.25 nm to 21.52 nm (Figure 5).

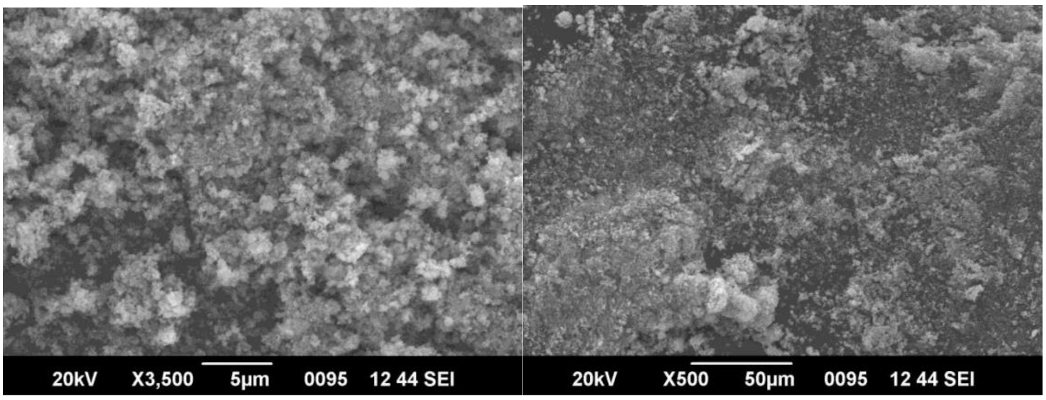

Figure 3. SEM image of cobalt manganese oxide nanomaterial prepared by sol-gel method.

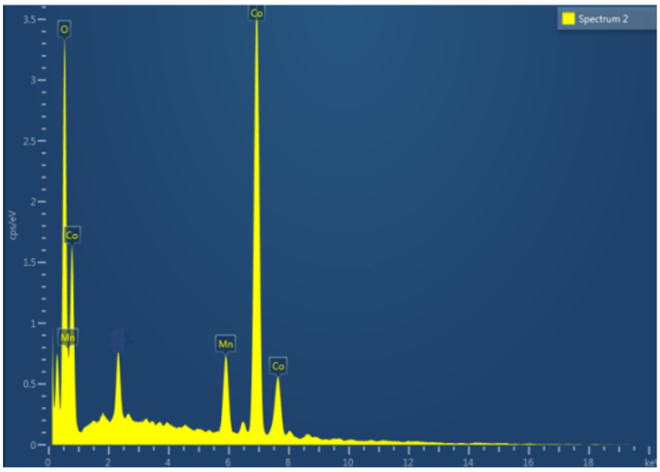

Figure 4. EDX of cobalt manganese oxide nanomaterial prepared by sol-gel method.

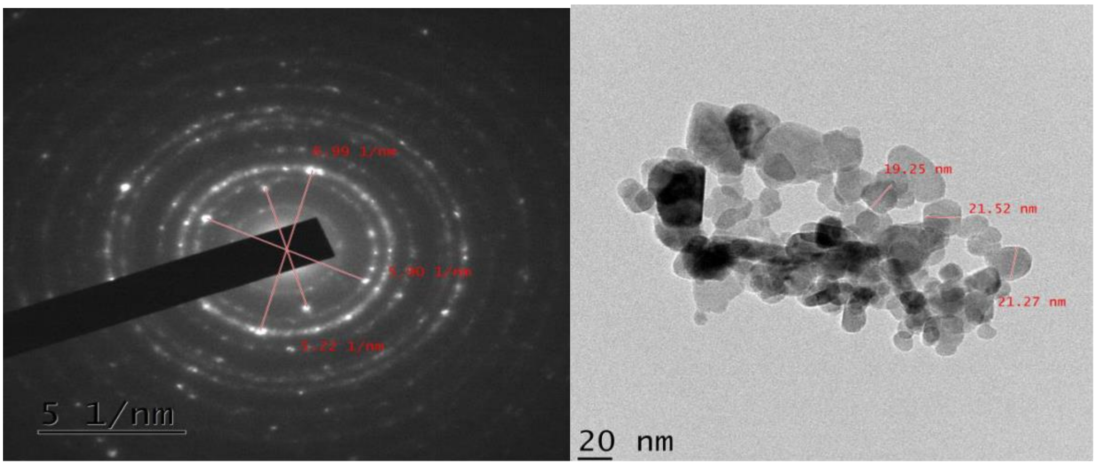

Figure 5. TEM of cobalt manganese oxide nanomaterial prepared by sol-gel method.

In recent years, nanomaterials had a wide range of applications in various fields. Some researchers have studied about use of nanomaterials for superior lithium-ion batteries and capacitors [15,22,29-31], a high-performance electrode for supercapacitors [23,32-36], Solid Oxide Fuel Cells [37], and photo-catalyst [16,38]. From these examples, we can say that $MnCo_2O_4$ spinel oxide nanomaterial is environmentally benign for living things and extremely useful in different fields.

4. Conclusions

Spherical-shaped $MnCo_2O_4$ spinel oxide nanomaterial was successfully synthesized using a sol-gel, an environmentally supportive method in this synthesis of binary Mn-Co nanomaterial, manganese chloride and cobalt chloride bind together using citric acid as a surfactant. We have used eco-friendly, cheap, easy handling, and harmless aqueous solvent systems in this method.

The FTIR analysis showed stretching vibrations of binary Mn-O and Co-O oxide in the spine. The XRD pattern indicates that the synthesized Mn-Co binary nanomaterial is homogeneous. The energy dispersive spectroscopy shows the presence of manganese, cobalt, and oxygen, as well as TEM, giving information about crystal size changes of manganese cobalt oxide nanomaterial. The spectroscopic studies confirmed that the absorption of binary Mn-Co oxide nanomaterial was determined from their morphologies.

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Conflicts of Interest

The authors declare no conflict of interest.

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