REVIEWS ON SYNTHESIS AND CHRACTERISATION OF METAL COBALTITES (MCo_2O_4)

A M.sc Dissertation report by:

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REVIEWS ON SYNTHESIS AND CHARACTERISATION
OF
METAL COBALTITES (MCo_2O_4)

A DISSERTATION REPORT

Submitted in partial fulfilment
Of
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By
MS. Purva Nagvekar

To the
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GOA UNIVERSITY
GOA 403505
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CERTIFICATE

This is to certify that " Reviews on synthesis and characterisation of metal cobaltites" is bonafide work carried out by Ms. Purva Nagvekar under my supervision in partial fulfilment of requirement for award of degree of Master of sciences in chemistry at the school of chemical sciences ,Goa university.

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secondly, I would also like to thank my parents and friends who helped me a lot in finalizing this project within the limited time frame.

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INTRODUCTION

Cobaltite is a significant mineral composed of cobalt, arsenic, and Sulphur (CoAsS) crystallizing in the orthorhombic (or pseudo cubic) system resembling pyrite. It contains up to 10% iron and a valuable amount of nickel. The name is derived from the German “Kobold” meaning “underground spirit” or “goblin” in allusion to the refusal of cobaltiferous ore to smelt appropriately. The colour changes from reddish silver-white, violet steel-grey to black with greyish-black streak and metallic lustre. The density is about 6.3. Cobaltite contains 35.5% Co, 45.2% As, and 19.3% S±Fe and Ni.[1]

In recent years, transition metal cobaltites have become a research hotspot in the field of electrochemistry due to their natural abundance, safety and low cost. There are many electrochemical application of transition metal cobaltites and their composites as electrode materials or as electrocatalysts in electrochemistry, such as supercapacitors (SCs), lithium-ion batteries (LIBs), electrocatalysts and electrochemical sensors, are introduced.[2]With the increasing amount of research on energy crises and environmental concerns, the study of environmentally friendly energy devices is critical for storing energy. Supercapacitors (SCs) are considered one of the most popular energy-storage devices because of their advantages such as high power density, long life span, excellent stability, cleanliness, and high efficiency .[3]

In this literature survey our topic of discussion is cobaltites, i.e., oxide compounds of cobalt, in which cobalt is in an oxidation state (charge state) of 3+. In these compounds, Co^{3+} ions can take the following spin configurations: high-spin, low-spin, and intermediate-spin configurations. The conditions for the formation of various spin states are given on the basis of the Tanabe–Sugano diagrams. X-ray spectral methods, such as X-ray photoelectron spectroscopy, X-ray emission spectroscopy, X-ray absorption spectroscopy, and X-ray magnetic dichroism, can be used to study cobaltites. By using X-ray absorption spectra, one can determine the charge and spin states of cobalt ions. These spectra can be reproduced by atom-like multiplet calculations that involve many electrons and use the energy splitting of atomic orbitals by the ligand field as a free parameter. In these compounds, cobalt ions are in tetrahedral positions and, consequently, trivalent cobalt ions should be exclusively in the high-spin state.

NICKEL COBALTITES ($NiCo_2O_4$)

Nickel cobaltite, $NiCo_2O_4$, generally has inverse spinel crystal structure. However, there are some evidence to suggest that , $NiCo_2O_4$ adopts an unusual magnetic structure in comparison to other inverse spinels owing to the variation in cation distribution. While it is generally accepted that Ni ions prefer to occupy octahedral sites, and Co ions are distributed in both octahedral and tetrahedral sites. since the, $NiCo_2O_4$ phase is thermally and structurally unstable above 673 K imposes the need for low temperature synthesis of the material. $NiCo_2O_4$ exhibits interesting magnetic behaviour with a Curie temperature T_c of approximately 673 K. The mono-dispersed nickel cobaltite nanoparticles at 473 K can be synthesised by a combustion route utilizing glycine as a fuel and nitrate as the oxidizer under nearly smouldering combustion conditions. Upon annealing such nanoparticles, we observed an interesting evolution of magnetic phase exhibiting unusual magnetic properties.[4]

Nickel cobaltite, $NiCo_20_4$, is of interest to electrochemists because it is a good catalyst for electrochemical oxygen reduction in an alkaline medium[5] .The high activity of nickel cobaltite in the oxidation of saturated, aromatic hydrocarbons and carbon monoxide allows its application as a catalyst for the neutralization of waste gases from diesel internal-combustion engines. In this connection, it is important to obtain a material with a high specific surface area.[6]

Due to the superior physical and chemical properties compared to their bulk materials, nanocrystals have attracted growing interest for both their fabrication and application. Therefore, morphologically controllable synthetic methods aiming for well-defined nanocrystals are the primary step. So far, the main synthesis strategies include liquid-phase co-precipitation, hydro- and solvothermal routes, microwave-assisted methods, electrodeposition methods, electrospinning methods and high temperature synthesis.[7]

Nickel cobaltite Nanoparticles can be synthesized through several methods such as hydrothermal synthesis, condensation using an inert gas, scattering. Each method results in the synthesis of a type of nanoparticle of specific characteristics which can be verified through X-ray diffraction (XRD), Fourier transform infrared analysis (FT-IR), and scanning electron microscopy (SEM).

The different characteristics such as the shape, size, and extent of formation of nanoparticles depend on certain parameters such as pH, incubation period, and temperature of the nanoparticle. Each of the methods of synthesis has merits and demerits. For example, hydrothermal synthesis needs expensive autoclaves, and reaction process is dangerous. The temperatures involved in the synthesis of nickel cobaltite nanoparticles via hydrothermal mechanism ranging from 200°C to 400°C, and the process of calcination in the furnace goes as high as even 600°C.

EXPERIMENTAL PROCEDURES

For the synthesis of nickel cobaltite

Ogale and co-workers reported on the synthesis of nearly monodispersed $NiCo_2O_4$ nanoparticles by a combustion method using glycine as a fuel and cobalt/nickel nitrates as oxidizer.[8]

$NiCo_2O_4$ was prepared by three different methods: by the thermal decomposition of carbonates and by sol-gel methods

a)by the thermal decomposition of carbonates

Stoichiometric amounts of commercial $CoCO_3$ and $NiCO_3 .2Ni(OH)_2. 4H_2O$ were thoroughly mixed in an agate mortar. The mixture was heated in oxygen at 3303°C for 24h.

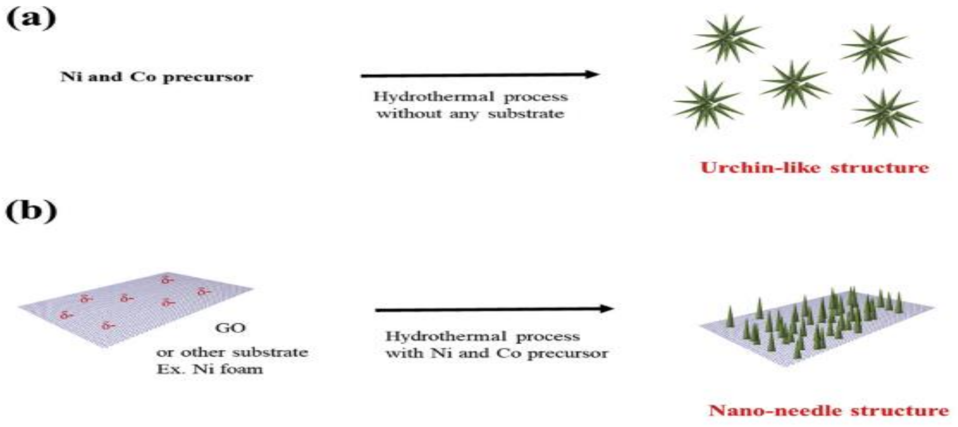
b) Sol-gel (SG).

A method similar to that used to prepare Co_3O_4 and other Ni-containing spinel was employed. Cobalt carbonate, $CoCO_3$, was freshly prepared by addition of sodium carbonate to a concentrated aqueous solution of cobalt chloride at 603°C. The precipitate was filtered, washed with hot water, and dried at 1003°C. The fresh $CoCO_3$, powder was mixed with a stoichiometric amount of nickel carbonate and dissolved in excess propionic acid. The solution was heated at 1403°C to evaporate the excess propionic acid and form a gel. Liquid nitrogen was added immediately to give a mixed nickel-cobalt propionate. This was subsequently heated at 2003°C for 2 h to remove the excess propionic acid. The product was finally grounded at 325 mesh and calcined in air at 3503°C for 24 h.[9]

C) Another method for the preparation of stoichiometric $NiCo_2O_4$ and Co-excess off-stoichiometric $Ni_{0.75}Co_{2.25}O_4$, $Ni_{0.88}Co_{2.12}O_4$ nanoparticles.

The reagents used are cobalt nitrate, nickel nitrate (extra pure,), glycine (AR,) was used as raw materials to prepare stoichiometric ($NiCo_2O_4$) and Co-excess off-stoichiometric (e.g., $Ni_{0.75}Co_{2.25}O_4$, $Ni_{0.88}Co_{2.12}O_4$ etc.) nickel cobaltite nano particles. various studies have shown that 0.5 mole of glycine per mole of metal is required for the synthesis of spinel phase nickel cobaltite nanoparticles. Based on this, an appropriate molar ratio of metal nitrates and glycine were mixed to obtain 10-15 g of stoichiometric and off stoichiometric nanoparticles. The resultant homogeneous solutions were slowly evaporated on a water bath to form a viscous gel. The gels were allowed to undergo rapid combustion reaction in a preheated furnace at 473 K. The samples were kept at the same temperature for 4h.

The synthetic method of preparation of cobaltite nano particles has many disadvantages like inert gas condensation is expensive and practically limited to the laboratory scale. In the inert gas condensation of nickel cobaltite nanoparticles, vaporization of the composite solution of Ni (II) and Co (II) in the ratio of 1:2 takes place in a thermal vaporization source like electron beam evaporators, or refractory crucibles, at pressures of 1-50 mbar. Coprecipitation is time consuming, inapplicable to species that have no charge and trace impurities and can also flocculate with the product . In the formation of nickel cobaltite nanoparticles by chemical coprecipitation, Ni (II) and Co (II) in the ratio of 1:2 are mixed, concentrated NaOH (2-8 M) solution is added, and the autoclaving follows at close to 300°C. Centrifuging is done to precipitate out the particles, precipitate is washed using distilled water to remove the neutral electrolyte, and then it is dried . Further these methods utilize chemicals that have toxicity in their nature in one way or the other and hence pose a risk to the environment and the livestock. hence there was a need for a greener method for the preparations of nano particles



D)Another method of synthesis of nickel cobaltite nanoparticles via the green route can be achieved with the help of (1) plants,

(2) naturally occurring biomolecules, and

(3) microorganisms.

For synthesizing nickel cobaltite nanoparticles by plants, the leaves of the plants are peeled off and boiled in distilled water. Then the solution of Ni (II) and Co (II) in the ratio of 1:2 is taken, and the boiled solution of plant extract is added to it. A change in the colour of the solution over a period of 3-4 days indicates the genesis of nanoparticles. Synthesizing nickel cobaltite nanoparticles with the aid of microorganisms, such as bacteria and fungi, on the other hand, is much economical and eco-friendly way .

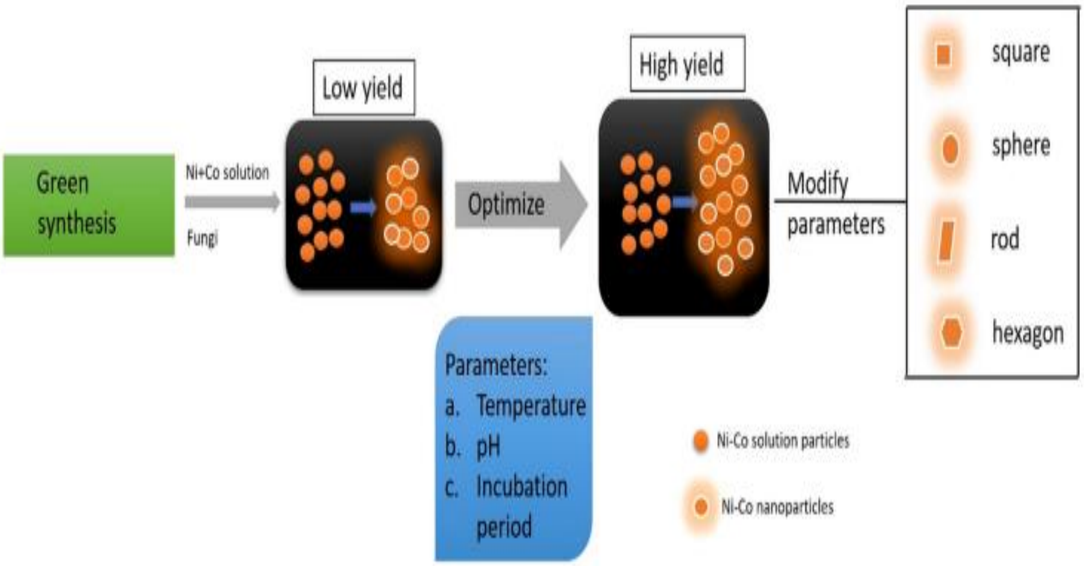
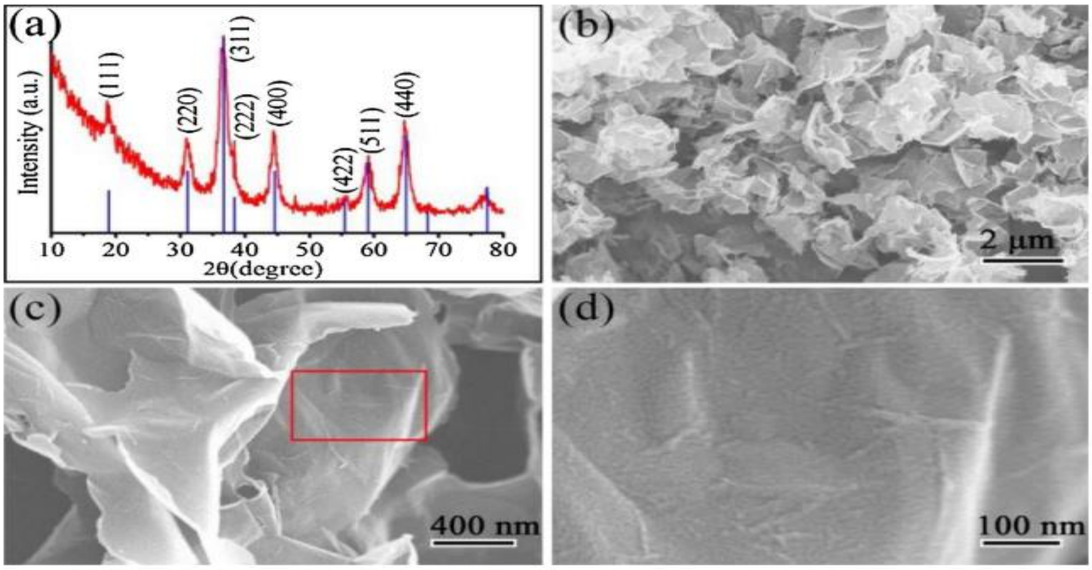


Fig1:- Mechanism of the biosynthesis of Ni-Co nanoparticles using fungi.

Therefore, among the method of preparation of nanoparticles, the use of microorganisms is the most cost effective and perennial way to produce the nanoparticles as they are abundant in nature and can be harvested in adverse conditions too. In addition, the synthesis of nanoparticles may also be done through biological route through microorganisms. It has become a suitable alternative to the conventional methods to synthesize nanoparticles . It is based on an eco-friendly and greener approach of producing nanoparticles that makes use of unicellular and multicellular organisms such as fungus, bacteria, viruses, yeast, and plants . These microorganisms can accumulate and remove the toxins from the heavy metals and metal composites that are to be reduced, such as nickel, cobalt, silver, and nickel cobaltite, with the help of the reductase enzymes, which reduce the metal and composite salts to corresponding nanoparticles.[10]

INTERPRETATION



The XRD pattern shows the main diffraction peaks are observed at 2u = 19.3, 31.1, 36.7, 44.6, 59.1, and 65.0°. All the diffraction peaks could be indexed to (111), (220), (311), (222), (400), (422), (511), and (440) crystal planes, respectively. This demonstrates that the as-synthesized sample belongs to cubic NiCo2O4 with a spinel crystalline structure. No characteristic peaks corresponding to other phase or impurities are observed, suggesting that the as-synthesized NiCo2O4 sample possesses high phase purity.

The SEM images clearly shows that the $NiCo_2O_4$ exhibits a sheet-like 2D structure. Their morphology is highly uniform, only nanosheets can be observed, no any other structure, such as fine nanoparticle and thick nanoplates exist.[11]

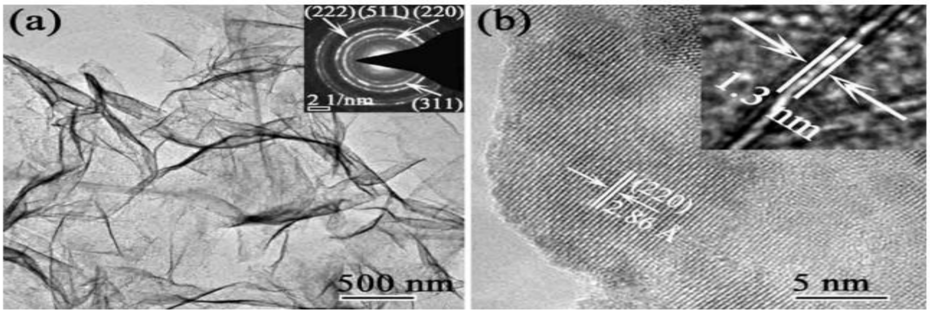


Fig (a) low-magnification TEM image of the $NiCo_2O_4$ nanosheets, which reveals the freestanding and large-area graphene-like morphology. (b) shows HRTEM image of the $NiCo_2O_4$ nanosheets. The spacing of the marked regular lattice fringes is calculated to be 2.86 Å, corresponding to the (2 2 0) plane of spinel $NiCo_2O_4$ phase.[11]

MANGANESE COBALTITE ($MnCo_2O_4$)

Manganese cobaltite spinel $Mn_xCo_3.xO_4$ ($0 < x < 1$), obtained by a synthetic route already applied to the preparation of high-density inorganic oxides, several ceramic materials and ZnO and CuO nanocrystals . Fine particle cobaltites have been characterized by X-ray powder diffraction, IR spectra, transmission electron microscopy, surface area and crystallite-size measurements.[12]

$MnCo_20_4$ has a cubic spinel structure $MnCo_20_4$ was synthesized by the ceramic method using the mixture of Mn_30_4 and Co_30_4 at the starting powders'[13].

A mesoporous flake-like manganese-cobalt composite oxide ($MnCo_2O_4$) is also synthesized successfully through the hydrothermal method. The flake-like $MnCo_2O_4$ is evaluated as the anode material for lithium-ion batteries. Owing to its mesoporous nature, it exhibits a high reversible capacity of 1066 mA h g^{-1} , good rate capability, and superior cycling stability. As an electrode material for supercapacitors, the flake like $MnCo_2O$ also demonstrates a high supercapacitance of 1487 F $^{g-1}$ at a current density of 1 A $^{g-1}$, and an exceptional cycling performance over 2000 charge/discharge cycles.[14]

One of the simpler and more cost-effective methods for obtaining high-quality, thick spinel films is screen-printing followed by thermal treatment. In this respect the “soft chemical” methods (glycine nitrate process (GNP).The second applied technique was coprecipitation, a simple, inexpensive and reliable method for the preparation of ceramic oxide powders. [15]

EXPERIMENTAL PROCEDURE

Materials used

Manganese(II) nitrate tetrahydrate $Mn(NO_3)_2.4H2O$ and cobalt(II) nitrate hexahydrate $Co(NO_3)_2.6H2O$ (SIGMA-ALDRICH, 99.999% trace metals basis) as starting materials and ethylenediaminetetraacetic acid (C10H16N2O8, ALDRICH, 99.995%) and ammonium hydroxide solution (28% NH3 in H2O, SIGMA-ALDRICH, 99.99% trace metals basis) as the chelating and precipitate agents, respectively. 2.

Preparation of $Mn_{1.5}CO_{1.5}O_4$ spinel powders.

Mn and Co nitrate solutions, which were subsequently mixed in the appropriate ratio to yield the desired stoichiometry. To obtain the gel precursor using the EDTA gel processes, the nitrate solution was mixed with a 0.1 M EDTA solution (ratio: 1 mol of EDTA per 1 mol of metal cations). Constant Ph= 8 was maintained via dropwise addition of ammonia. The aqueous solution containing manganese and cobalt complexes was slowly heated and stirred at 70 to 80°C to evaporate the water until a transparent glassy gel was obtained. The gel precursor was then pyrolyzed at 600°C for 1 h, crushed, and calcinated at 800°C for 10 h in static air.

In the coprecipitation technique the nitrate solution was added into a concentrated ammonium hydroxide solution. The obtained gel was dried at room temperature for 24 h and then at 100°C for 2 h. The dried gel was calcinated at 800°C for 10 h in static air. The two resulting types of powders were ground in a rotarye vibratory mill in dry ethanol with some amount of PVD for 5 h and finally dried at room temperature. To prepare bulk samples 10 mm in diameter and about 2 mm in height, the powders were isostatically pressed under 250 MPa and afterward the green bodies were sintered at 1150°C in static air for 12 h with a heating rate of 5°C min.[16]

INTERPRETATION

FTIR spectra of $MnCo_2O_4$ nanoparticles as seen in Fig1, the sharp peaks at 458 and 523 cm for pure $MnCo_2O_4$ can be attributed to the metal-oxygen bonds in tetrahedral and octahedral sites in the spinel lattice, respectively. adsorption of MO by nano spinel's caused Co–O bands to shift to high wavenumber, and the bands at 1642 and 1092 cm^{-1} became stronger, indicating the presence of interaction among $MnCo_2O_4$ MO adsorption.[17]

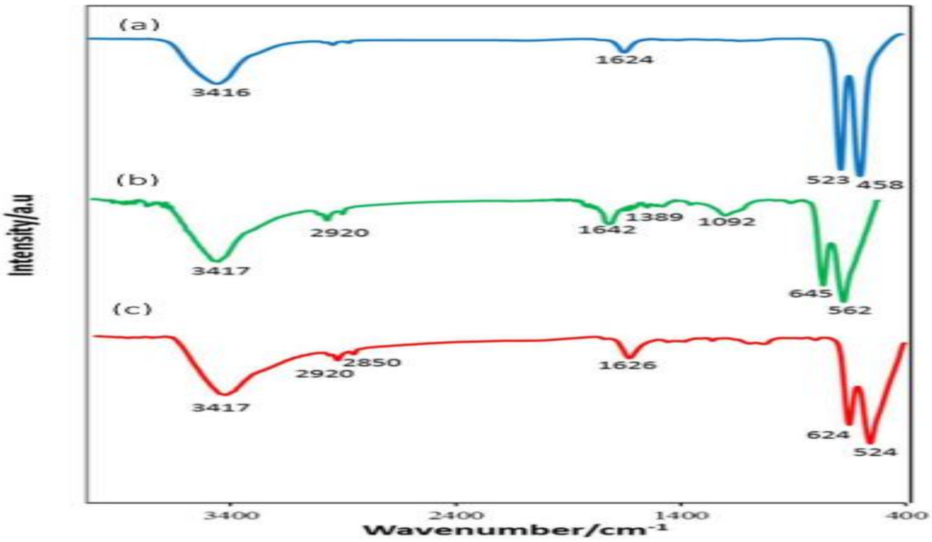


Fig 1 :- FT-IR spectra of MnCo2O4 nano spinel's (a), MnCo2O4 after

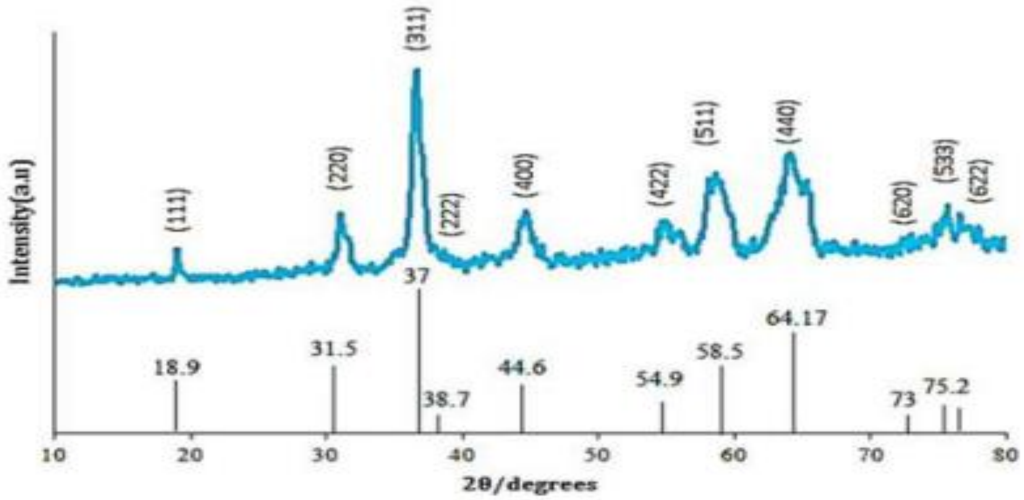


Fig2:- . XRD pattern of prepared MnCo2O4 nano spinel

The diffraction peaks match with cubic $MnCo_2O_4$ crystal lattice. without detectable impurities. The average crystallite size diameter (D) of the nanoparticles has been estimated by Debye–Scherrer equation

D=0.9λ/βcosϴ

Where D is the crystal size, λ (= 0.15418 nm) is the wavelength of X-ray, θ is the diffraction angle of the peak (311) of MnCo2O4, and β represents the half-height width after subtracting the apparatus broadening effect (FWHM). The Crystallite size of the MnCo2O4 has been founded to be about 40 nm.[17]

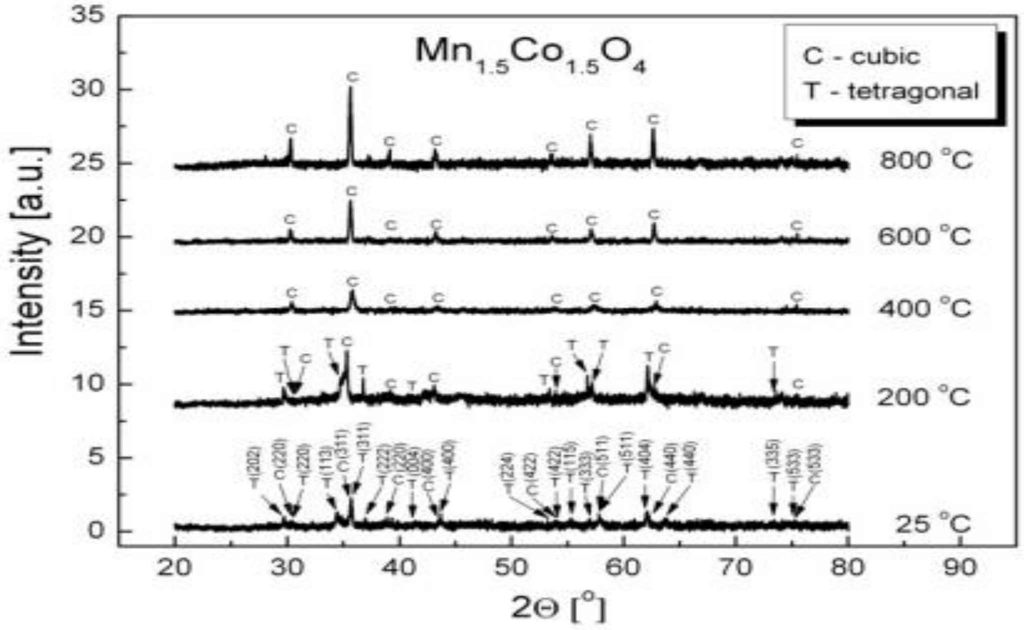


Fig3:- High temperature X-Ray diffraction pattern for $Mn_{1.5}Co_{1.5}O_4$ samples.

The x-ray diffraction pattern for $Mn_{1.5}Co_{1.5}O_4$ bulk samples prepared using EDTA gel processes and sintering green bodies at 1150°C for 12 h in air. As we can see, the presence of the tetragonal spinel phase in the manganese cobaltite spinel containing both the cubic and tetragonal phases selectively decreases with temperature. This phase disappears at 400 °C and only the cubic spinel phase is then observed (Fig. 3). This phase transformation is due to reduction of Co and Mn cations to lower valences, migration of these cations from octahedral interstices to tetrahedral ones and the loss of oxygen. Similar observations were made for for $Mn_{1.5}Co_{1.5}O_4$ bulk samples prepared by coprecipitation. For spinels with the formula MMn_2O_4 (where M=Mn, Mg, Zn, Cd, Co and Fe), exhibit tetragonal cubic transition with temperature. The ratios between the intensities of reflections of the cubic and tetragonal phases, i.e., reflections (220) and (113), respectively, for the two types of $Mn_{1.5}Co_{1.5}O_4$ bulk samples , suggests that these ratios are higher for powders prepared via EDTA gel processes for both investigated temperatures.

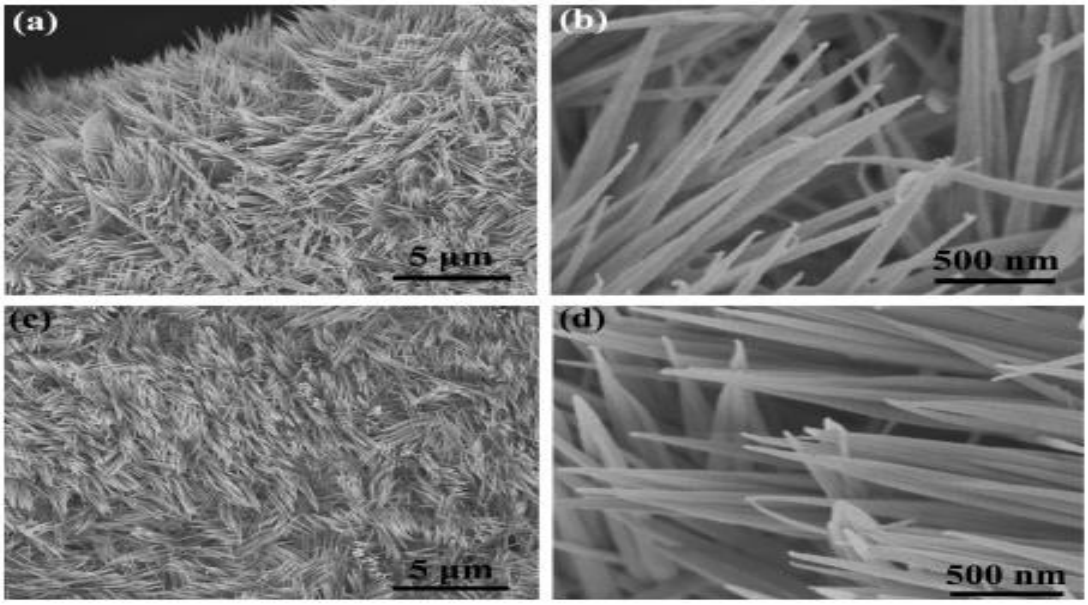


fig4:- SEM images of the as-prepared $MnCo_2O_4$

The SEM images show the nanowires with an average diameter of 70 nm grows in direction on the nickel foam forming nanowire arrays (Fig. 4a,4b). The morphologies of the $MnCo_2O_4$ nanowires and their cobalt-manganese hydroxide precursor (Fig.4c,4d) before annealing are almost the same maintaining the nanowire structure. Further insight into the detailed nanostructure is elucidated by TEM (Fig.5), further confirming the nanowire architecture. The MnCo2O4 nanowires present a mesoporous structure, which is ascribed to the successive release and lose of CO_2 and H_2O during the thermal decomposition of the precursor.[18]

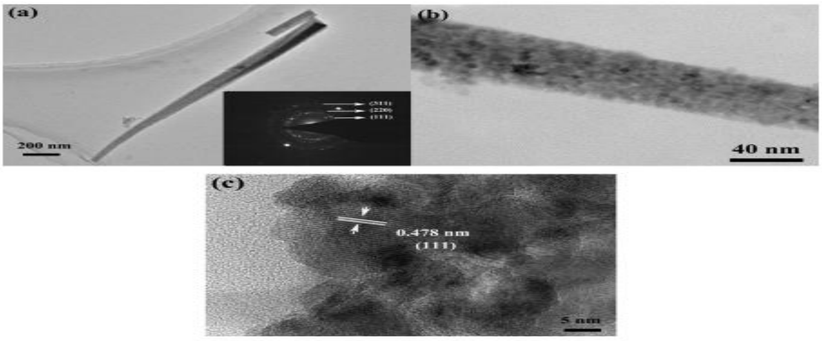


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Fig5:-TEM images for $MnCo_2O_4$

CADMIUM COBALTITE ($CdCo_2O_4$)

Composite solid propellants (CSPs) are the major source of chemical energy in space vehicles and missiles . Ammonium perchlorate (AP) is the most common oxidiser in CSPs, in which it plays a significant role in the burning process. Thermal decomposition of AP can be improved to some extent by reducing the particle size of AP, decreasing the particle size of AP is a dangerous process [4]. 5-Nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO) is an insensitive high-energy compound that has potential applications as an oxidiser in CSPs. This compound is highly useful in non-azide inflating propellant compositions for automobile air bags . 1,3,5,7- Tetranitro-1,3,5,7-tetraazacyclooctane, commonly known as HMX, is one of the more powerful high explosives used in military applications ,such as in the detonator in nuclear weapons, in the form of plastic-bonded explosives and as a solid rocket propellant. Thermal decomposition characteristics of HMX, NTO and AP influence the combustion behaviour of the propellants. The properties of CSPs can be improved by adding a catalyst, such as metal oxides or metal ferrites etc., that accelerates the rate of decomposition of AP. Recent investigations have shown that nanoparticles of transition metals, metal oxides and cobaltites (3d series) can increase the burning rate .

EXPERIMENTAL PROCEDURES

Synthesis of $CdCo_2O_4$ nanoparticles (CCNs) by co precipitation method

CCNs were synthesised at room temperature by dissolving 0.01 M of $Cd(NO_3)_2$ and 0.02 M of $Co(NO_3)_2$ in 150 mL deionised water to obtain a mixed metal nitrate solution and the molar ratio of nitrates was fixed to be 1:2. The other precipitant used was NaOH solution (2.0 M, 50 mL). NaOH was introduced under vigorous magnetic stirring and gave a blue-coloured precipitate of metal hydroxides. After complete precipitation, the colour changes from blue to brown within 15–20 minutes. The brown precipitated product was washed with distilled water two times and then ethanol two times to make it free of nitrate ions, was dried overnight at 100°C and then calcined at 300°C in air for 10 hours to afford CCNs.[19]

INTERPRETATION

X-ray diffraction (XRD; Figure 1) were performed on an X-ray diffractometer using Cu-K_{α} (λ=¼ 1.5418A) radiation.

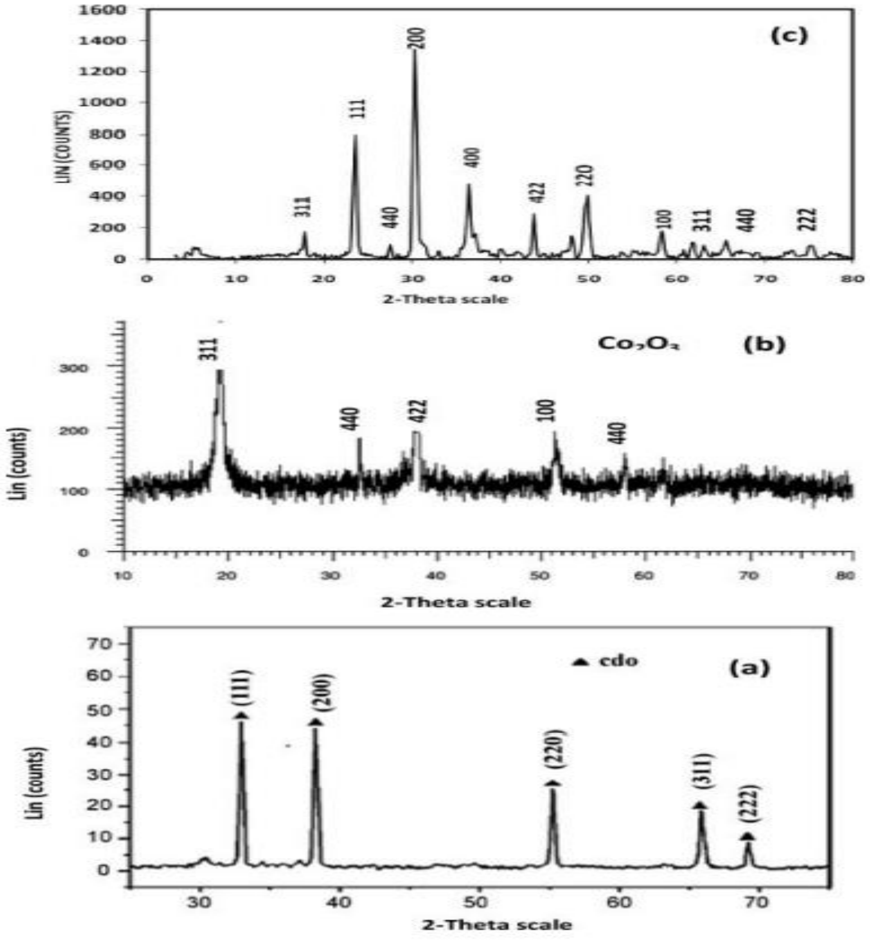


Fig 1:-XRD FOR $CdCo_2O_4$

Figure 1 shows the structural characteristics of CCNs investigated by XRD. The broadening of the peaks indicates the nanometre size of the products and no peak of impurity was observed in the XRD pattern. The relative crystalline size of CCNs is estimated to be 27 nm from the XRD line broadening using the Scherrer equation . For comparison, XRD patterns of pure CdO (curve a) and Co_2O_3 (curve b) nanoparticles prepared by the co-precipitation method are also shown in Figure 1. The diffraction peaks in the for $CdCo_2O_4$ catalyst of curve (c) slightly shifted at the 2u scale. There were no observable lines in the XRD spectra corresponding to those of pure CdO and Co_2O_3 nanoparticles. If pure for $CdCo_2O_4$ was not formed, in curve (c), diffraction peaks of pure CdO or Co_2O_3 would have been observed at the same 2u value. This provides evidence for the formation of pure for $CdCo_2O_4$ nanoparticles. The morphology and structure of the calcined sample was characterised by FE-SEM. From the FE-SEM and TEM images (Figure 2a–d), it is found that the morphology of CCNs is generally spherical, with a diameter of 20–30 nm. The result indicates that the average size (20–30 nm) is matched well with the estimated size obtained from the XRD.[19]

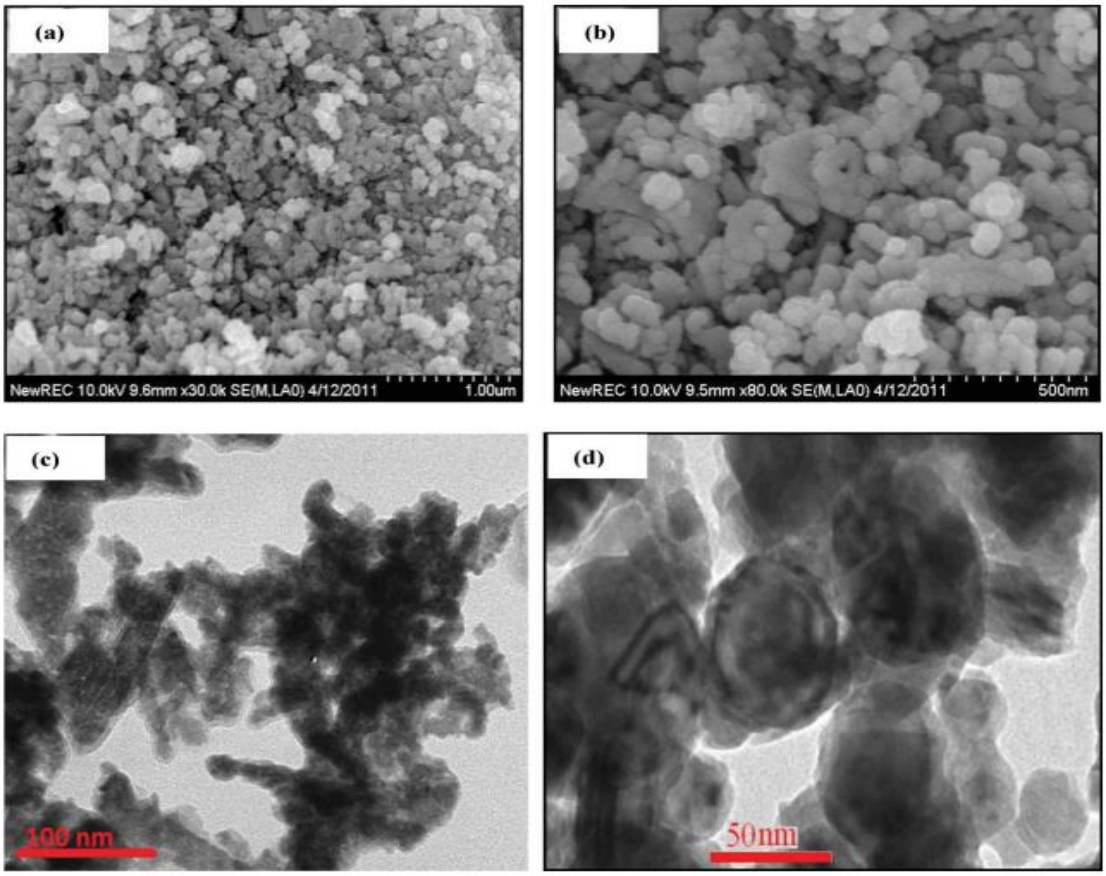


Fig2:-SEM(a,b) and TEM(c,d) for $CdCo_2O_4$ nanoparticles

The size and morphology of the sample was observed on field electron scanning electron microscope (FE-SEM). FE-SEM analysis, the sample was distributed over the sample holder using the carbon tape and then air was used to remove the non-attached particles on the holder. Before placing into the sample chamber, a thin Pt layer was deposited on the powder sample for achieving good-quality images of powder samples. The particle size and the distribution of CCNs were determined using transmission electron microscopy (TEM). For TEM analysis, a pinch of powder sample was dispersed into the solvent (ethanol) through sonication .Afterwards, a Cu grid was dipped into the dispersed samples and dried at 60°C for 10 minutes. This Cu grid was placed on the JEOL JEM TEM sample holder and put into the sample chamber for analysis.

ZINC COBALTITE ($ZnCo_2O_4$)

Porous zinc cobaltite (**$ZnCo_2O_4$**) microspheres have been successfully prepared by a facile solvothermal method followed by an annealing process. The prepared **$ZnCo_2O_4$** displays uniform sphere-like morphology composed of interconnected **$ZnCo_2O_4$** nanoparticles. The surface area of mesoporous **$ZnCo_2O_4$** microspheres is about 51.4 m^2 g^{-1} with dominant pore diameter of 7.5 nm. The superior electrochemical performance is mainly attributed to the uniformity of the surface structure and the porosity of the micro spheres, which benefit electrons and ions transportation, provide large electrode-electrolyte contact area, and meanwhile reduce volume change during the charge discharge process. This method of constructing porous microspheres is very effective, yet simple, and it could be applied in other high performance metal oxide electrode materials for electrochemical capacitors, as well as in Li-ion batteries.

EXPERIMENTAL PROCEDURES

Synthesis of mesoporous $ZnCo_2O_4$.

All chemicals used was of analytical grade and used without further purification. The formation process of the mesoporous **$ZnCo_2O_4$** microspheres was based on a solvothermal method followed by an annealing process. In this typical procedure, 1 mmol of $Zn(NO_3)_2.6H_2O$ and 2 mmol of $Co(NO_3)_2.6H_2O$ were added into 30 mL of absolute ethanol to form a solution. Then 5 mL of 1.2 M $(NH_4)_2CO_3$ aqueous solution was added with vigorous stirring. The reaction mixture was then transferred into a Teflon-lined stainless-steel autoclave with a capacity of 50 mL, heated in an oven at 150°C for 6 h, and then allowed to cool to room temperature naturally. The pink precursor was collected by centrifugation and washed with water and ethanol for several times, before drying at 60°C for 12 h. The thermal decomposition of the precursor for producing mesoporous **$ZnCo_2O_4$** microspheres was performed in a furnace at 400°C for 2hr.

INTERPRETATION

The crystallographic information of samples was obtained by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500 powder diffractometer (Cu Ka radiation, l ¼ 0.15418 nm). The morphologies were characterized by the field emission scanning electron microscopy (FESEM; JEOL JSM-6700F), the transmission electron microscope (TEM) and high-resolution TEM ((HRTEM; Tecnai G2 F20).

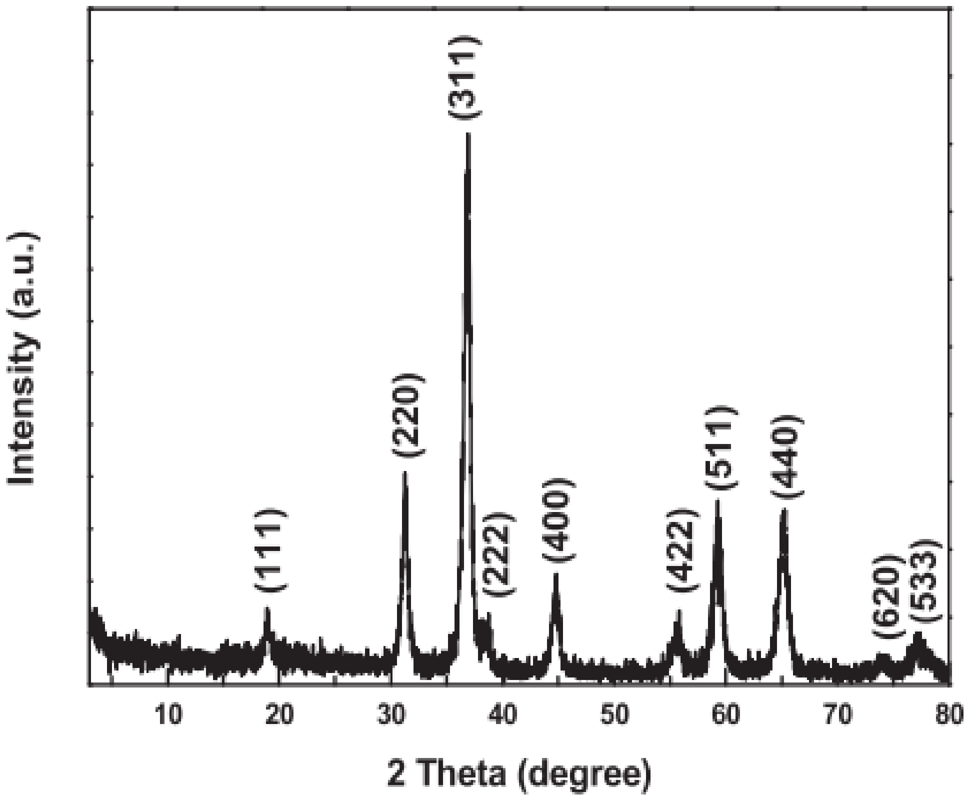


Fig1:-xrd pattern of as prepared mesophorous $ZnCo_2O_4$ microspheres

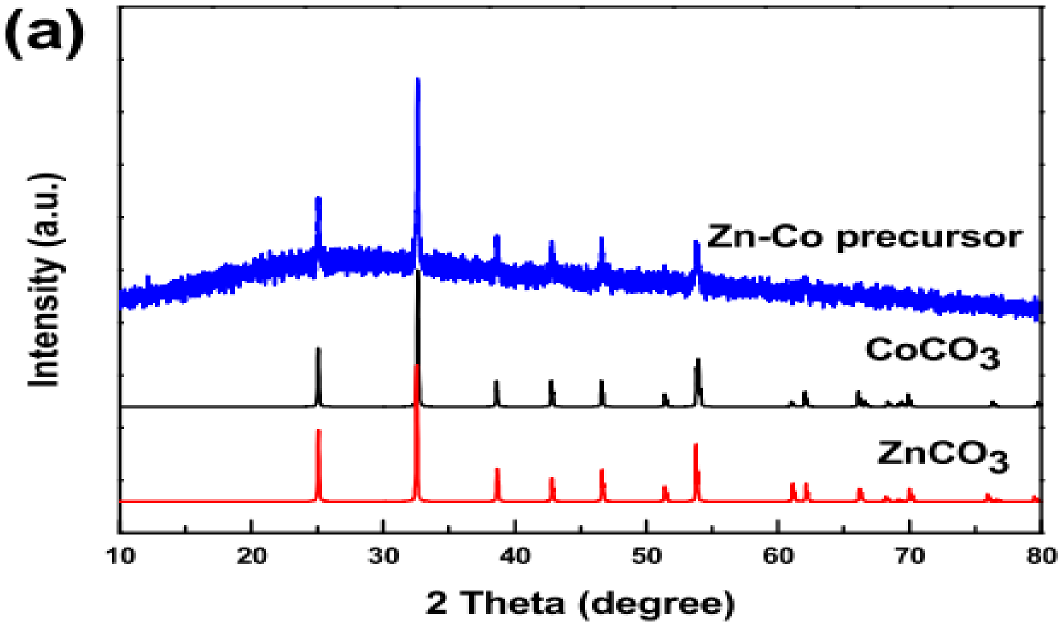


Fig2:-xrd pattern of Zn-Co precursor

The XRD peaks shown in Fig. 1a indicate the formation of the $ZnCO_3$-$CoCO_3$ precursor.

No more detectable peak from impurity is observed in the XRD pattern, demonstrating the complete transformation of the precursor to the spinel **$ZnCo_2O_4$**. Moreover, the relatively high peak intensities imply that the **$ZnCo_2O_4$** spheres are highly crystalline. It is obvious the (311) peak has the highest intensity, indicating the oriented growth of the sample in the (311) direction.

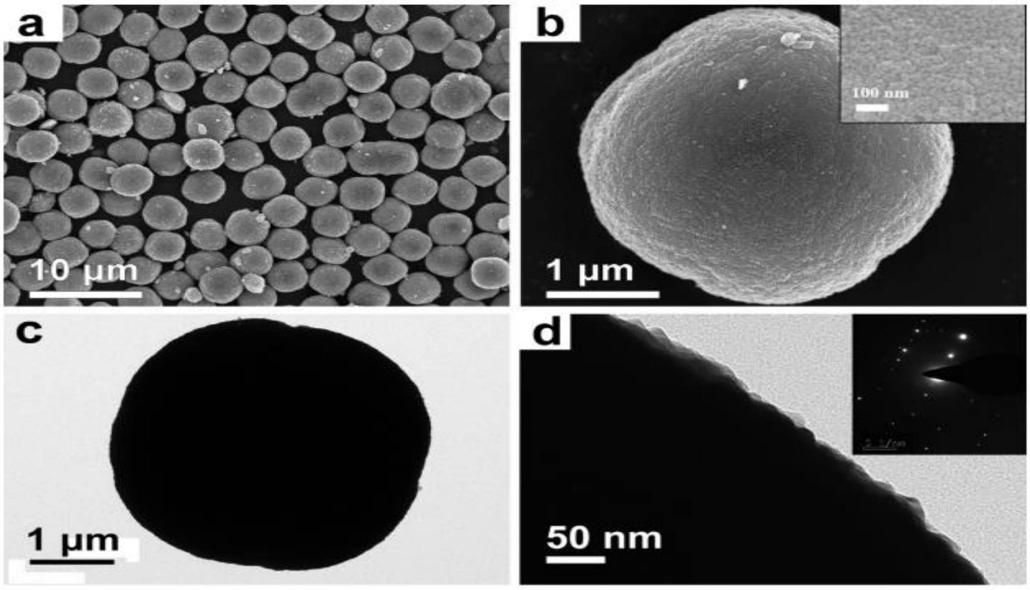


Fig- 3. SEM images (a-b), TEM images and SAED pattern (c-d)

The morphology and the microstructure of the resultant mesoporous **$ZnCo_2O_4$** microspheres were characterized by SEM and TEM. The SEM image shown in Fig. 3a reveals that the product is composed of uniform mono-dispersed microspheres with the size of 3-4 mm in diameter, which is similar to the Zn-Co precursor. The magnified view of the microspheres shown in Fig. 3b displays inerratic heaves like litchi shells on the surface of the **$ZnCo_2O_4$** microspheres. The SEM image from the surface of a microsphere (Fig. 3b) reveals that the **$ZnCo_2O_4$** microsphere is composed of numerous primary nanoparticles (NPs). The surface of the **$ZnCo_2O_4$** microspheres is rougher than that of the Zn-Co precursor, which is ascribed to the release of CO_2 gas during the decomposition of the Zn-Co precursor. Likewise, from the TEM image shown in Fig. 3c, a high uniformity of the microspheres with rough surface can be observed. And the porosity of the **$ZnCo_2O_4$** microspheres is clearly seen from the edge of a single sphere (Fig. 3d). It can be found that numerous nanoparticles are closely packed and held together as a whole, demonstrating the existence of pores.

BARIUM COBALTITE ($Ba_2Co_9O_{14}$)

$Ba_2Co_9O_{14}$ is a polycrystalline thermoelectric semiconductor with the capability of making oxygen vacancies. $Ba_2Co_9O_{14}$ has a proper electronic conductivity . Subsequently, it could competitively be used with the traditional cathode material. Ban+1cono3n+3 (Co8O8)compound can be synthesized in a solid-state microprobe(synthesized by. Ehora et al.). In this method, BaO_2 and CoO was used as precursors, and its magnetic properties was investigated . $Ba_2Co_9O_{14}$ has significant properties, . Roll et al synthesized barium cobalt in a solid-state micro-scale, and used it for the first time as a cathode in a solid oxide fuel cell . Takami et al. Synthesized a combination of sodium bicarbonate and lanthanum doped barium cobalt with solid-state micro-scale, and investigated its thermoelectric properties . Delorme et al. Investigated the combination of barium cobalt with solid-state synthesis and thermoelectric properties of this material .[20]

EXPERIMENTAL PROCEDURES

Synthesis

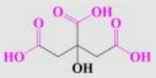
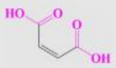
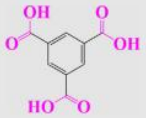
Sol-gel procedure and the Pechini technique gives benefits of uniform metal/citrate complexes, lower costs, homogeneous compositions, low calcination temperature, and insensitivity against humidity. The method was done based on the creation of metal citrate complexes. $Ba_2Co_9O_{14}$ nanoparticles is a novel nanomaterial for the hydrogen storage by a simple and cost-effective and straightforward chemical method.

Materials used

All the used chemical reagents in this study were used without further refinement. $Ba(NO_3)_2$ and $Co(NO_3)_2.6H_2O$ applied as barium source and cobalt source, respectively. The acid source and propylene glycol are used as a gel-forming agent.

Synthesis of $Ba_2Co_9O_{14}$ nanoparticles using the pechini method

To prepare the $Ba_2Co_9O_{14}$ nanoparticle, various acid sources such as citric acid, maleic acid, and Trimesic acid were utilized. In this procedure, 0.1145 mmol of $Ba(NO_3)_2$, 0.5153 mmol of $Co(NO_3)_2.6H_2O$, and 0.0006 mmol of citric acid dissolved in a small amount of deionized water. These solutions were mixed thoroughly via a magnetic stirring at ambient temperature. Then propylene glycol was added into the mixture to form a sol at 50 C for 1 h and then further heated to create the gel. The molar ratio of propylene glycol to citric acid was 1:1. The obtained gel was dried in a vacuum oven at 60 ——————————— C for 5 h, and then it powdered using a grinder. Finally, the resultant powder was used as a precursor and calcined at 900 C for 4 h. [20]

Sample No.	Type of acid source	Type of diol	Chemical structure
1	Citric acid	Propylene glycol	
2	Maleic acid	Propylene glycol	
3	Trimesic acid	Propylene glycol	

Scheme 1 – Schematic illustration of the preparation of the synthesized $Ba_2Co_9O_{14}$ nanoparticles by the Pechini method at 900 °C.

INTERPRETATION

FT-IR spectrum was applied to investigate the purities and functional groups of the surface of the nanoparticles. Fig. 1 illustrates the FT-IR spectra of $Ba_2Co_9O_{14}$ nanoparticles in the presence of citric acid, maleic acid, and Trimesic acid. the bands at 3439-3430 cm^{-1} and 1625-1628 cm^{-1} corresponds to n (O-H) stretching and bending vibration.

For the pure Ba2Co9O14 nanoparticle, the XRD peaks are at 2q ¼ 31.6712°, 32.9684°, 33.0753°, 36.7972°, 39.0096°, 41.4955°, 42.8767°, 44.7091°, 48.7229°, 56.0265°, 59.5690°, 65.6157°. The stated angles at the XRD patterns are related to the phase of $Ba_2Co_9O_{14}$ with Hexagonal crystal structure and lattice parameters of a=b=5.6960 A and c=28.9240 A. The average crystallite diameter estimated for synthesized nanoparticles by Debye-Scherrer equation (D =0.9 k/bcosλ) calculated approximately 25 nm.

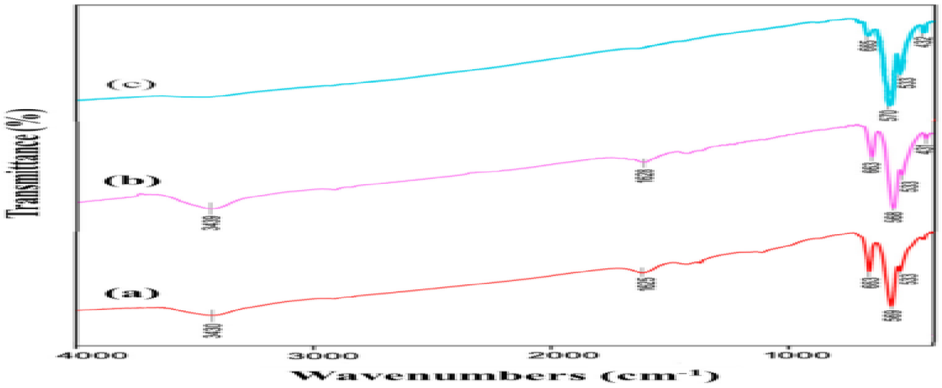


Fig. 1:- FT-IR spectra of the synthesized $Ba_2Co_9O_{14}$ nanoparticles: (a) sample no. 1, (b) sample no.2, and (c) sample no. 3

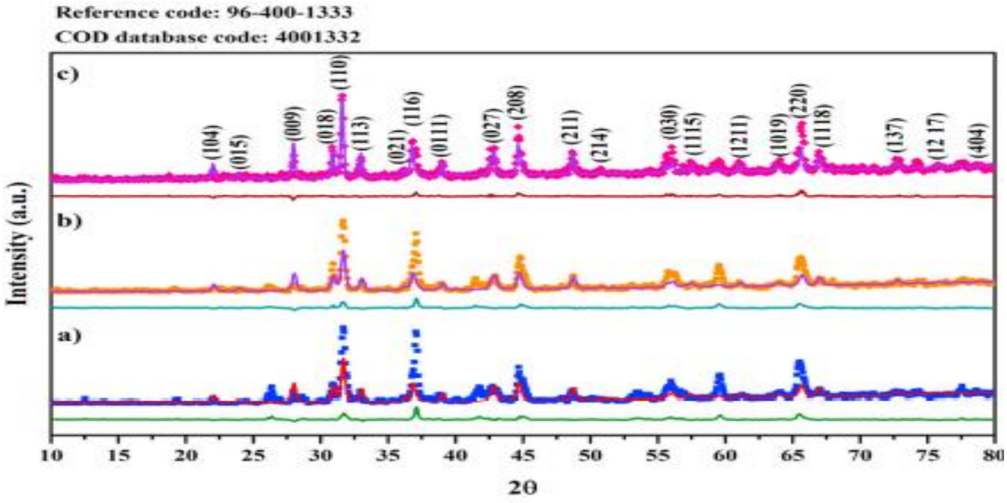


fig.2:- XRD patterns of the synthesized $Ba_2Co_9O_{14}$ nanoparticles by different acid sources: (a) citric acid, (b) maleic acid, and (c) Trimesic acid.

SEM and TEM

In fig 3 we can see that when citric acid was selected as an acid source, the $Ba_2Co_9O_{14}$ structure was mainly formed of tiny and small nanoparticles with homogeneous morphology .By changing the acid source to maleic acid, it can see that aggregated nanoparticles are created . Also, using Trimesic acid as an acid source increased the particle size .This various in morphology is due to the difference in their structure (Table 1) and the steric hindrance effect . The citric acid shows better performance than Trimesic acid and maleic acid due to more steric hindrance.

Fig4 shows that the TEM images of synthesized $Ba_2Co_9O_{14}$ nanoparticles that contain nanoparticles with diameters ranging from 14 to 25 nm in different magnifications.

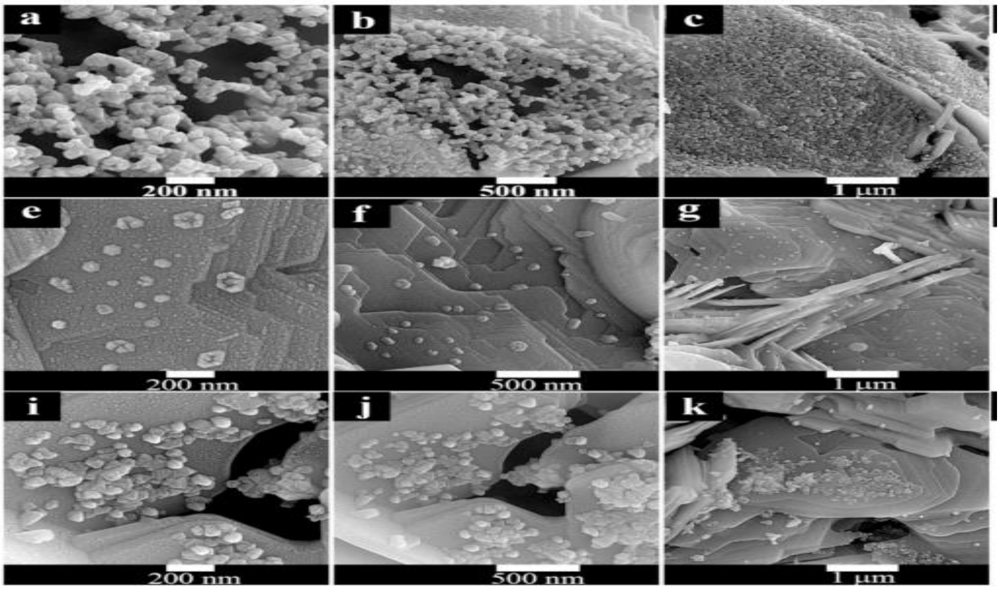


fig. 3 - SEM images of the synthesized $Ba_2Co_9O_{14}$ nanoparticle by different acid sources, (a-c) citric acid, (e-g) maleic acid, and (i-k) Trimesic acid in different scales

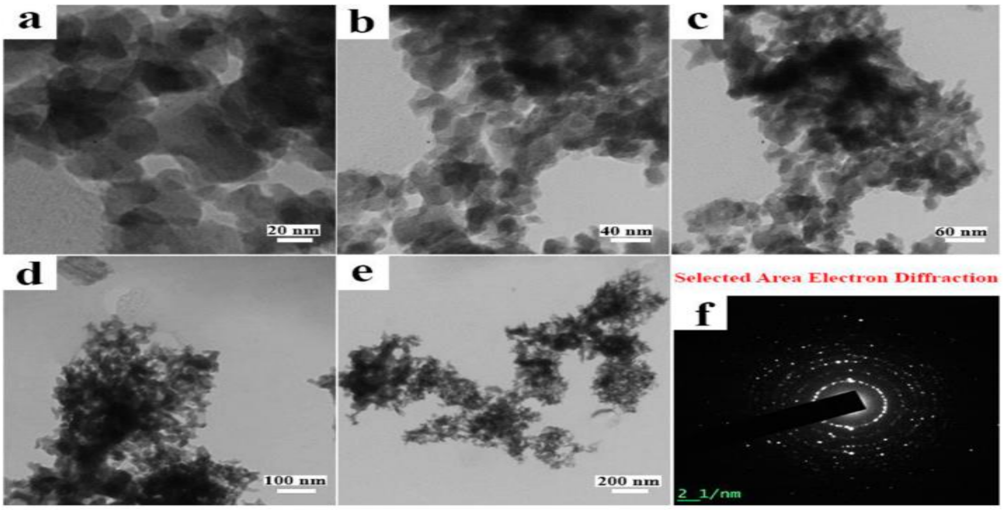


Fig. 4:- TEM images of the synthesized $Ba_2Co_9O_{14}$ nanoparticle by citric acid in different scales (a-e), and selected area electron diffraction (SAED) pattern (f).

APPLICATIONS

There are many application of cobaltite nano particles .

1. Nickel cobaltites

It is worth that $NiCo_2O_4$ (NCO) is not only low in cost, but also environmentally friendly. NiCo2O4 was used as a candidate for SCs. Researcher has reported that different chelating agents have a substantial influence on the pore structure, particle sizes and specific surface areas of $NiCo_2O_4$. This simple, economical and high-performance strategy allows $NiCo_2O_4$ as a SC electrode to have broad application prospects. In recent years, researchers have expended considerable efforts to improve the electrochemical performance of NiCo2O4 electrodes. Jiang et al. produced a porous $NiCo_2O_4$ nanoplate by a two-step synthetic method, which saved time and cost, and obtained a specific capacitance of 1362 F g-1 when the current density was 1 A g-1. The simplicity and practicality of this method means $NiCo_2O_4$ has potential application prospects in the field of energy storage. Wang et al. also reported good electrochemical performance by $NiCo_2O_4$.[2]

NCO is believed to exhibit an inverse spinel structure with Ni cations occupying the octahedral sites while Co cations are evenly distributed to both the octahedral and tetrahedral sites. However, Ni ions can diffuse into the tetrahedral sites substituting Co, which is reported to cause changes in lattice constants and magnetic moments. NCO is also known to have ferrimagnetic order with magnetization of 1.71lB per formula unit under a field of 10 T at 4 K.[22]

Due to unique combination of electrical conductivity, infrared transparency, electro catalytic activity, and ferrimagnetic order, spinel $NiCo_2O_4$ (NCO) is widely utilized for various technological applications including transparent conducting oxides, bifunctional catalyst for oxygen evolution, reduction in alkaline media, and water electrolysis.

2. Manganese cobaltite

$MnCo_2O_4$ Manganese-based oxides are easy to obtain, low cost, and low in toxicity, and can be applied in many fields. The application of $MnCo_2O_4$ in SCs is in the initial stage. The mixed valence $MnCo_2O_4$ has shown excellent catalytic performance for oxygen reduction reactions. A $MnCo_2O_4$ material that combines redox active Co and Mn species in three-dimensional nanostructure remains to be well explored in CO_2 photoreduction catalysis. Using the $MnCo_2O_4$ microspheres as a cocatalyst, the catalytic performance of the conversion of CO_2 to CO was remarkably promoted.[23]

Spinel-type oxides ($MnCo_2O_4$) have also is an promising OER alternatives for noble metals oxides in alkaline electrolyte solutions because of their excellent redox properties, multiple valence states, it also show certain electrocatalytic performance, which can be further improved by several strategies, such as surface modification with conducting poly pyrrole, amorphous Mn-Co-P shell, or supporting on conductive carbon substrates (e.g., graphene, carbon nanotubes), but their electrocatalytic performance is still far from satisfied. Recently, investigators have reported that CeO_2-decorated or incorporated electrocatalysts could exhibit promising performance with low overpotentials and excellent stability for OER and HER, which have been attributed to the facilitated electron transfer between Ce^{3+}/Ce^{4+} and active sites, improved stability in an alkaline electrolyte, high oxygen transfer to the reaction sites, high oxygen storage capacity and modified local chemical binding.[24]

cobalt containing manganese spinel oxides have been considered a potential candidate for applications in research areas such as catalysis, sensors, electrode materials and electrochemical devices due to their excellent physicochemical and enhanced electrochemical properties. $MnCo_2O_4$ demonstrates excellent pseudocapacitive behaviour due to combined effects of Mn^{2+} and Co^{3+} cations. While cobalt shows a higher oxidation potential, manganese can transport more electrons and achieve a higher capacitance.[25] .To improve the electrochemical performances of $MnCo_2O_4$ various morphological structures such as flowers, flakes, sticks and fibres have been designed and synthesized. Che and coworks assembled flower-like $MnCo_2O_4$ hollow microspheres with numerous ultrathin nanosheets as the petals. Pettong et al. prepared $MnCo_2O_4$ nanofibers (NFs) for application in asymmetric supercapacitors (ASCs), and the cyclic voltammetry (CV) . The CV voltammograms show that the shape and redox potential of the materials can affect the scan rate. An ASC made from $MnCo_2O_4$ NFs//N-doped reduced graphene oxide aerogel (N-rGO) showed an excellent specific capacitance, which can be used as a high power energy storage device.

3.Other metal cobaltites

A large number of studies have shown that transition metal cobaltites usually obtains excellent performance due to its relatively special structure, and have great application prospects in SCs. For example, a porous network structure composed of nanowires enables the material to have a high specific surface area and a suitable pore volume, thereby making it easier for the electrolyte to penetrate the nanowires, improving the utilization of the active material. In addition, bimetallic organic framework materials also provide faster kinetic performance through synergistic effects between ions and rich redox reactions.. The specific capacitance of the electrode material in an SC is very important for improving the energy storage of SCs. To improve their specific capacitances, the structures of transition metal cobaltites is key. In recent years, to obtain electrode materials with better performance, researchers have tried to design and synthesize transition metal cobaltites with various structures and have continuously tried to combine transition metal cobaltites with other materials to further improve their electrical conductivities. It is believed that in the near future, transition metal cobaltites will be put into practical use as the electrode material of SCs.

CONCLUSIONS

In this present study ,many method has been adopted to prepare different cobaltites ($NiCo_2O_4$, $MnCo_2O_4$, $CdCo_2O_4$, $ZnCo_2O_4$, $BaCo_2O_4$, $Ba_{0.5}La_{0.5}Co_{3-\gamma}$) nanoparticles. Comparison of different cobaltite can be made. The qualities of the all the cobaltites differ significantly from each other. The results was characterized by FTIR, XRD,SEM,TEM which gives information about different types of streaching vibrations, their crystallise size, morphology, phases etc.. This article has reviewed the research progress of transition metal cobaltite materials and their composites in SCs, LIBs, electrocatalysis and electrochemical sensors in recent years. From the existing syntheses and applications, the transition metal cobaltites and their composite materials can exhibit excellent capacities, cycle lifetime, and rate capabilities. However, there are still several disadvantages such as poor conductivities and stabilities. In recent years, researchers have combined transition metal cobaltites with other materials, such as graphene and that have excellent electrical conductivities. This not only overcomes the drawbacks of the transition metal cobaltite materials themselves, but also results in exhibits superior electrochemical performances. By combining transitional cobaltite materials with materials with good electrical conductivities, it has been shown that such hybrid materials can exhibit improved performances in a number of other applications. Because the electrochemical performances of the materials are improved, they have broad application prospects in their industrial application to energy storage devices. In addition to applications in electrochemical fields, such as SCs, batteries, electrocatalysts and electrochemical sensors, transition metal cobaltite materials can be used for water purification, gas separation and storage.

REFRENCES

[1] S. K. Haldar, “Introduction,” *Platinum-Nickel-Chromium Deposits*, pp. 1–35, Jan. 2017, doi: 10.1016/B978-0-12-802041-8.00001-8.

[2] X. Guo, C. Chen, Y. Zhang, Y. Xu, and H. Pang, “The application of transition metal cobaltites in electrochemistry,” *Energy Storage Materials*, vol. 23. Elsevier B.V., pp. 439–465, Dec. 01, 2019. doi: 10.1016/j.ensm.2019.04.017.

[3] C. C. Yang, W. C. Sun, A. Kumar, B. Pattanayak, and T. Y. Tseng, “Templating synthesis of nickel cobaltite nanoflakes and their nanocomposites for making high-performance symmetric supercapacitors,” *Materials Today Energy*, vol. 14, Dec. 2019, doi: 10.1016/j.mtener.2019.100356.

[4] S. Verma, A. Kumar, D. Pravarthana, A. Deshpande, S. B. Ogale, and S. M. Yusuf, “Off-stoichiometric nickel cobaltite nanoparticles: Thermal stability, magnetization, and neutron diffraction studies,” *Journal of Physical Chemistry C*, vol. 118, no. 29, pp. 16246–16254, Jul. 2014, doi: 10.1021/jp504538y.

[5] Y. Shen, D. Kan, I. C. Lin, M. W. Chu, I. Suzuki, and Y. Shimakawa, “Perpendicular magnetic tunnel junctions based on half-metallic NiCo2O4,” *Applied Physics Letters*, vol. 117, no. 4, Jul. 2020, doi: 10.1063/5.0017637.

[6] D. G. Klissurski and E. L. Uzunova, “Synthesis of Nickel Cobaltite Spinel from Coprecipitated Nickel-Co balt Hydroxide Carbonate,” 1991.

[7] S. Liu, L. Hu, X. Xu, A. A. Al-Ghamdi, and X. Fang, “Nickel Cobaltite Nanostructures for Photoelectric and Catalytic Applications,” *Small*, vol. 11, no. 34. Wiley-VCH Verlag, pp. 4267–4283, Sep. 01, 2015. doi: 10.1002/smll.201500315.

[8] M. Cabo, E. Pellicer, E. Rossinyol, O. Castell, S. Suriñach, and M. D. Baró, “Mesoporous NiCo2O4 spinel: Influence of calcination temperature over phase purity and thermal stability,” *Crystal Growth and Design*, vol. 9, no. 11, pp. 4814–4821, Nov. 2009, doi: 10.1021/cg900648q.

[9] J. F. Marco, J. R. Gancedo, M. Gracia, J. L. Gautier, E. Ríos, and F. J. Berry, “Characterization of the nickel cobaltite, NiCo2O4, prepared by several methods: An XRD, XANES, EXAFS, and XPS study,” *Journal of Solid State Chemistry*, vol. 153, no. 1, pp. 74–81, 2000, doi: 10.1006/jssc.2000.8749.

[10] N. Srivastava *et al.*, “Microbial synthesis of nickel-cobaltite nanoparticle for biofuel applications,” in *Recent Developments in Bioenergy Research*, Elsevier, 2020, pp. 349–362. doi: 10.1016/B978-0-12-819597-0.00018-0.

[11] Y. Zhu and C. Cao, “A Simple Synthesis of Two-Dimensional Ultrathin Nickel Cobaltite Nanosheets for Electrochemical Lithium Storage,” *Electrochimica Acta*, vol. 176, pp. 141–148, 2015, doi: 10.1016/j.electacta.2015.06.130.

[12] J. L. Martin De Vidales, O. Garcfa-Martinez, E. Vila, R. M. Rojas, and M. J. Torralvo, “LOW TEMPERATURE PREPARATION OF MANGANESE COBALTITE SPINELS [inxCo3.xO 4 (0 <: x ~; 1)],” 1993.

[13] N. Yamamoto, S. Higashi, S. Kawanoi", and N. Achiwat, “Preparation of MnCo204 by a wet method and its metal ion distribution,” 1983.

[14] A. K. Mondal, D. Su, S. Chen, A. Ung, H. S. Kim, and G. Wang, “Mesoporous MnCo2O4with a flake-like structure as advanced electrode materials for lithium-ion batteries and supercapacitors,” *Chemistry - A European Journal*, vol. 21, no. 4, pp. 1526–1532, Jan. 2015, doi: 10.1002/chem.201405698.

[15] T. Brylewski, A. Kruk, A. Adamczyk, W. Kucza, M. Stygar, and K. Przybylski, “Synthesis and characterization of the manganese cobaltite spinel prepared using two ‘soft chemical’ methods,” *Materials Chemistry and Physics*, vol. 137, no. 1, pp. 310–316, Nov. 2012, doi: 10.1016/j.matchemphys.2012.09.026.

[16] T. Brylewski, A. Kruk, A. Adamczyk, W. Kucza, M. Stygar, and K. Przybylski, “Synthesis and characterization of the manganese cobaltite spinel prepared using two ‘soft chemical’ methods,” *Materials Chemistry and Physics*, vol. 137, no. 1, pp. 310–316, Nov. 2012, doi: 10.1016/J.MATCHEMPHYS.2012.09.026.

[17] S. Tarighi and N. M. Juibari, “Green Synthesized Manganese-Cobaltite Nanospinel and Its Dye Removal Characteristics: Isothermal and Kinetic Studies,” *ChemistrySelect*, vol. 4, no. 21, pp. 6506–6515, Jun. 2019, doi: 10.1002/slct.201900816.

[18] L. Li *et al.*, “One-dimension MnCo2O4 nanowire arrays for electrochemical energy storage,” *Electrochimica Acta*, vol. 116, pp. 467–474, Jan. 2014, doi: 10.1016/j.electacta.2013.11.081.

[19] S. Singh, P. Srivastava, I. S. Kapoor, and G. Singh, “Synthesis, characterisation and catalytic activity of cadmium cobaltite nanoparticles: part 87,” *Journal of Experimental Nanoscience*, vol. 10, no. 1, pp. 29–44, Jan. 2015, doi: 10.1080/17458080.2013.788225.

[20] F. S. Razavi, M. Hajizadeh-Oghaz, O. Amiri, M. S. Morassaei, and M. Salavati-Niasari, “Barium cobaltite nanoparticles: Sol-gel synthesis and characterization and their electrochemical hydrogen storage properties,” *International Journal of Hydrogen Energy*, vol. 46, no. 1, 2021, doi: 10.1016/j.ijhydene.2020.09.196.

[21] I. Szpunar *et al.*, “Electric and magnetic properties of lanthanum barium cobaltite,” *Journal of the American Ceramic Society*, vol. 103, no. 3, pp. 1809–1818, Mar. 2020, doi: 10.1111/jace.16865.

[22] P. Silwal, L. Miao, I. Stern, X. Zhou, J. Hu, and D. Ho Kim, “Metal insulator transition with ferrimagnetic order in epitaxial thin films of spinel NiCo 2O 4,” *Applied Physics Letters*, vol. 100, no. 3, Jan. 2012, doi: 10.1063/1.3676439.

[23] S. Wang, Y. Hou, and X. Wang, “Development of a stable MnCo2O4 cocatalyst for photocatalytic CO2 reduction with visible light,” *ACS Applied Materials and Interfaces*, vol. 7, no. 7, pp. 4327–4335, Feb. 2015, doi: 10.1021/am508766s.

[24] X. Huang *et al.*, “Enhanced Water Splitting Electrocatalysis over MnCo 2 O 4 via Introduction of Suitable Ce Content,” *ACS Sustainable Chemistry and Engineering*, vol. 7, no. 1, pp. 1169–1177, Jan. 2019, doi: 10.1021/acssuschemeng.8b04814.

[25] S. Sahoo, K. K. Naik, and C. S. Rout, “Electrodeposition of spinel MnCo2O4 nanosheets for supercapacitor applications,” *Nanotechnology*, vol. 26, no. 45, Oct. 2015, doi: 10.1088/0957-4484/26/45/455401.