

VIBRATIONAL PROPERTIES OF COBALT OXIDE NANOPARTICLE BY CO-PRECIPITATION METHOD

Dr.K.Ezhumalai¹.,Dr.K.N.Chadambarakumar².,Dr.R.Purushothaman³.,Ms.R.Jayasri⁴.

Assistant professor
Department of physics
Dhanalakshmi Srinivasan College of arts and science for women (autonomous)
Perambalur- 621212

Abstract

Nanotechnology refers to the creation and utilization of materials whose constituents exist at the nanoscale; and, by convention, be up to 100 nm in size. Nanotechnology explores electrical, optical, and magnetic activity as well as structural behavior at the molecular and submolecular level. The absorption band at 567 cm^{-1} was assigned to Co-O stretching vibration mode and 661 cm^{-1} was assigned to the bridging vibration of O-Co-O bond denotes the $\text{Co}^{2+}\text{Co}^{3+}\text{O}_3$ bonding vibrations as in type ABO_3 (where A denotes the Co^{2+} in the tetrahedral site) of the crystal lattice structure[7]. The small broad band at 3440 cm^{-1} is due to O-H stretching vibration modes. The less intense band at 1635 cm^{-1} is assigned to the bending mode of water molecule vibration. Increasing the calcination temperature reduces the intensity of the 3440 cm^{-1} , which may be due to the reduction in water content of the samples.

Key Words: Cobalt oxide nanoparticles,FTIR,RAMAN

1.1 Introduction

Nanotechnology can be defined as research and technology development at the atomic, molecular or macro molecular levels in the length scale of approximately 1-100 nanometers [1]. The idea of nanotechnology was first recognized by noble prize winner, an American scientist Richard Feynman who said “There is plenty of room at bottom”. There are endless possibilities for improved devices, structures and materials if we can understand these differences and learn how to control the assembly of small structures. Nanotechnology, which is one of the novel technologies, discusses to the development of structures, devices and systems having size 1-100 nm [2].

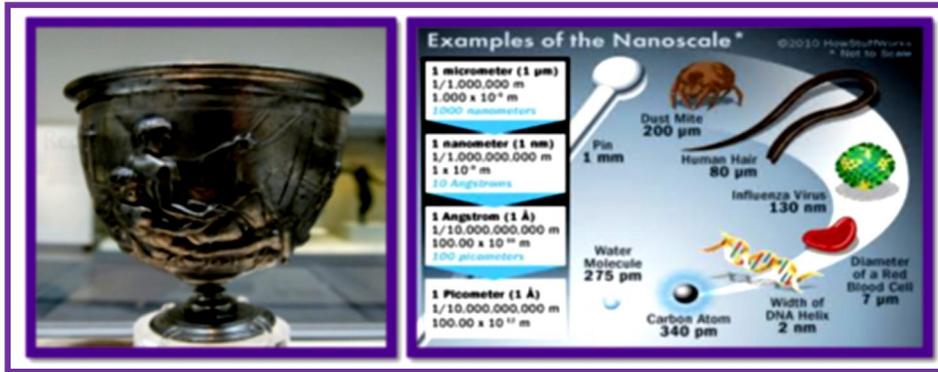


Fig. 1.1: Examples of nanotechnology and nanoscale materials

Nanotechnology used to reduce the cost of catalysts used in fuel cells. It can be used in sensors to detect elements such as carbon nanotubes, zinc oxide nanowire based on the sensor. It is used in medicine to reduce damage to healthy cells in the body and allows for earlier detection of disease. Ex: chemotherapy [1].

1.2. Classification of nanomaterials

1.2.1. According to the dimensions

Zero dimensional: These nanomaterials have nano dimensions in all the three directions.

Metallic nano particles including gold and semiconductor such as quantum dots are the perfect examples. Most of these nanoparticles are spherical in size and the diameter of these particles will be in the 1 – 50 nm range.

One dimensional: These nanostructures of one dimension will be outside the nanometer range. These include nano wires, nano rods and nano tubes. These materials are long (micrometer in length), but with diameter of only a few nanometer. Nanowire and nanotubes of metals, oxides are few examples. Fig. 1.3 shows the classification of nanomaterials under dimensions.

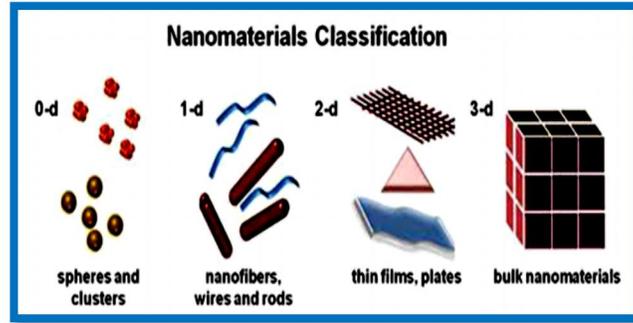


Fig. 1.2: Classification of nanomaterials under dimensions

Two dimensional: This type of nanomaterials also outside the nanometer range. These include different kind of nanofilms such as coatings and thinfilm – multilayer nano sheets or nanowalls. The area of the nanofilms can be large, but the thickness is always in nano scale range.

Three dimensional: All dimensions of these are outside the nanometer range. These include bulk materials composed of the individual blocks which are in the nanometer scale.

1.2.2. On the basis of structural configuration

Carbon based nanomaterials: The nature of this kind of nanomaterials is hollow spheres, ellipsoids or tubes. Spherical and ellipsoidal configured carbon nanomaterials are defined as fullerenes, while cylindrical ones are described as nanotubes. Fig. 1.3 shows the classification of nanomaterial under structural configuration [3].

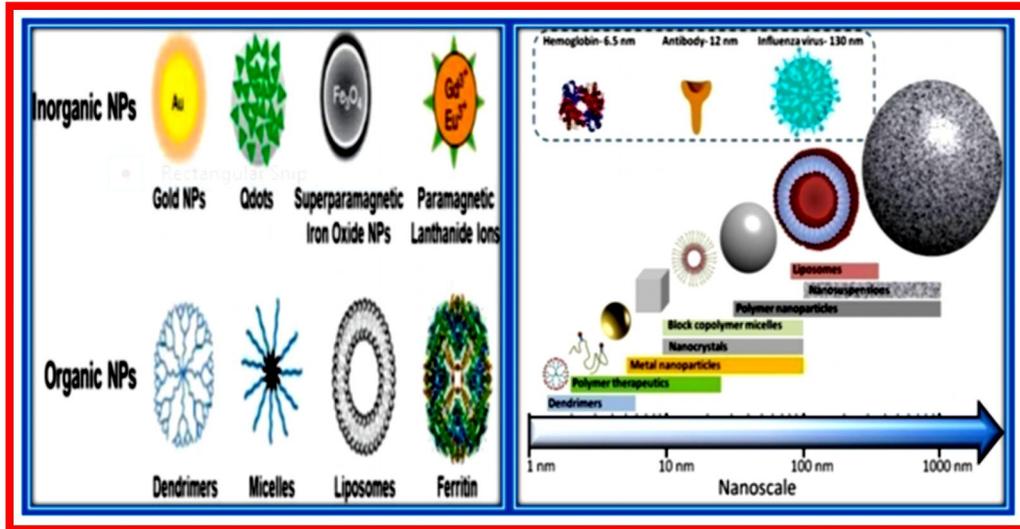


Fig. 1.3: Classification of nanomaterial under structural configuration

1.3. Properties of nanomaterials

1.3.1. Physical properties

- Large fraction of surface atoms.
- Large surface energy.
- Spatial confinement.
- Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to reduced probability of defects.

1.3.2. Chemical properties

Chemical properties of nanomaterials also change at nano scale. As the percentage of surface atoms in nano particles is large compared with bulk objects, therefore reactivities of nanomaterials are more than bulk materials.

- The preponderance of surface is a major reason for the change in behavior of materials at the nanoscale. As up to half of all the atoms, properties such as electrical transport are no longer determined by solid state bulk phenomenon.

1.3.3. Magnetic properties

- Magnetic nanoparticles are used in a range of applications like imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media.
- The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties.

1.3.4. Optical property

- In small nano clusters the effect of reduced dimensionality on electronic structure has the most profound effect on the energies of highest occupied molecular orbital (HOMO) which is valence band the lowest unoccupied molecular orbital (LUMO), essentially the conduction band.
- The optical emission and adsorption occurs between these two states.
- Semiconductor and many metals show large change in optical properties such as color, as a function of particle size [1].

1.4. Applications of nanomaterials

- **Cosmetics application of nanoparticle:** E.g. sunscreen lotions: (reabsorb properties).

- **Nanocomposites:** Nanoparticle silicate nanolayer (clay nanocomposites) and nano tubes can be used as reinforced filler not only to increase mechanical properties of nanocomposites but also to import new properties (optical, electronic etc).
- **Nanocoatings:** Surface coating with nanometer thickness of nanomaterial can be used to improve properties like wear and scratch-resistant, optoelectronics, hydrophobic properties.
- **Hard cutting tools:** Current cutting tools (e.g. mill machine tools) are made using a sort of metal nano composites such as tungsten carbide, tantalum carbide and titanium carbide that have more wear and erosion-resistant, and last longer their conventional (large-grained) materials.

1.5. Material introduction

1.5.1. Cobalt (II, III) oxide

Cobalt (II, III) oxide is an inorganic compound with the formula Co_3O_4 . It is a black antiferromagnetic solid. As a mixed valence compound, its formula is sometimes written as $\text{Co}^{\text{II}}\text{Co}_2^{\text{III}}\text{O}_4$ and sometimes as $\text{CoO} \cdot \text{Co}_2\text{O}_3$. Cobalt has two stable oxide states known as CoO and Co_3O_4 . At room temperature both compounds are found to be kinetically stable. Co_3O_4 is an important magnetic p-type semiconductor having direct optical band gaps as 1.48 and 2.19 eV. Co_3O_4 adopts the normal spinel structure, with Co^{2+} ions in tetrahedral interstices and Co^{3+} ions in the octahedral interstices of the cubic close packed lattice arrays of oxide anions as shown in Fig. 1.5. Cobalt (II, III) oxide structure and cobalt (II) oxide structure are shown in the Fig. 1.4. As a result, the Co^{3+} ions are not magnetic, whereas the Co^{2+} ions carry a magnetic moment. Co_3O_4 is a paramagnetic semiconductor at room temperature. It becomes antiferromagnetic below T_N

~40K, where the antiferromagnetism is mainly due to the weak coupling between nearest neighbour Co^{2+} ions [3].

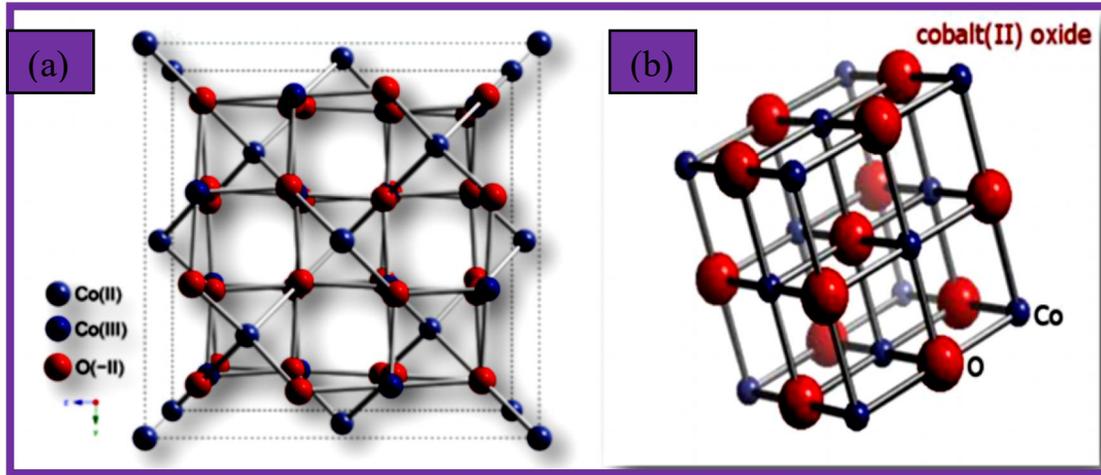


Fig. 1.4: (a) Cobalt (II, III) oxide structure, (b) Cobalt (II) oxide structure

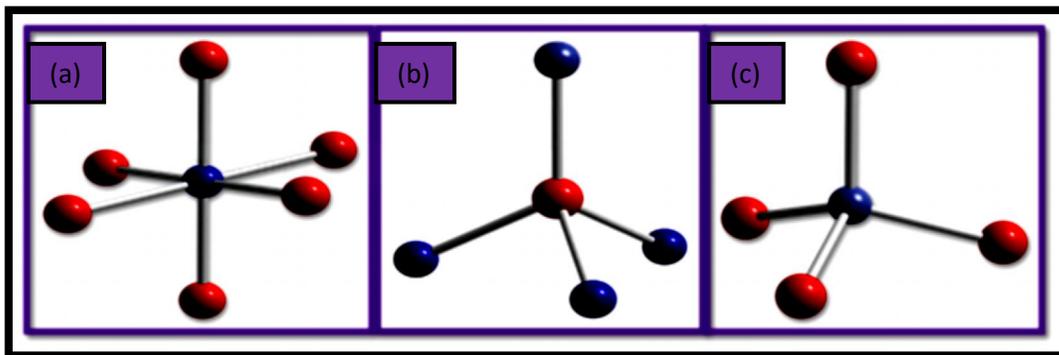


Fig. 1.5: a) Tetrahedral co-ordination geometry of Co(II) , b) Distorted octahedral co-ordination geometry of Co(III) and c) Distorted tetrahedral co-ordination geometry of O

SYNTHESIS METHODS AND CHARACTERIZATION TECHNIQUES

2.1. Introduction

Nanocrystalline materials can be synthesized either by consolidating atoms/molecules/clusters or breaking down the bulk material into smaller and smaller dimensions. The former is known as the “Bottom up” approach, whereas, the latter is referred to as the “Top down” method. Many techniques including both Top-down and Bottom up approaches have been developed and applied for the synthesis of nanoparticles. In the Top-down approach a block of a bulk material is whittled or sculptured to get the nanosized particle. The Top-down approaches include milling or attrition, lithography etc. The main disadvantage of Top-down approach is the imperfection of the surface structure. The nanoparticles produced by the attrition have a relatively broad size distribution and various particle shape or geometry. In addition they may contain significant amount of impurities. In the Bottom-up approach, the individual atoms and molecules are placed or self assembled precisely where they are needed. Here the molecules or atomic building blocks fit together to produce nanoparticles. Bottom-up approaches are more favorable and popular in the synthesis of nanoparticles and many preparation techniques of Bottom-up approach have been developed. Fig. 2.1 shows two approaches of synthesis of nanoparticles. Some of the chemical methods for the synthesis of nanoparticles are discussed in following sections.

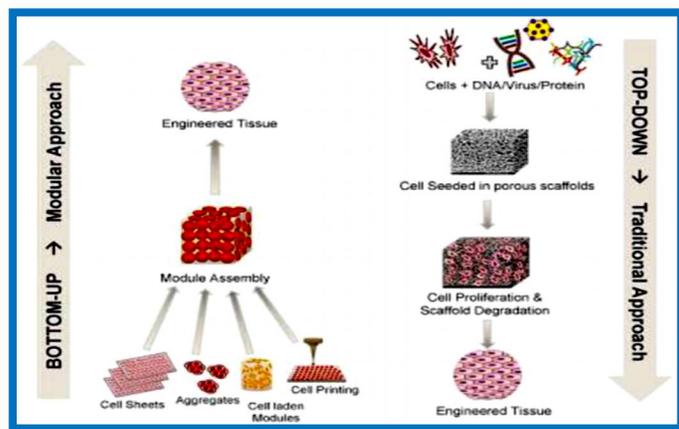


Fig. 2.1: Two approaches of synthesis of nanoparticles

2.2. Co-precipitation method

In this process, the required metal cations from a common medium are co-precipitated usually as hydroxides, carbonates, oxalates, formates or citrates. These precipitates are subsequently calcinated at appropriate temperatures to yield the final powder. For achieving high homogeneity, the solubility products of the precipitate of metal cations must be closer. Co-precipitation results in atomic scale mixing and hence, the calcining temperature required for the formation of final product is low, which lead to lower particle size. However, each synthesis requires its own special conditions, precursor reactions, etc. Also co-precipitation process required to control the concentration of the solution, pH, temperature and stirring speed of the mixture in order to obtain the final product with required properties.

Advantages of co-precipitation method

- Homogeneous mixing of reactant precipitates reduces the reaction temperature.
- Simple direct process for the synthesis of fine metal oxide powders, which are highly reactive in low temperature sintering.

Disadvantages of co-precipitation method

- This process is not suitable for the preparation of high pure, accurate stoichiometric phase.
- This method does not work well, if the reactants have very different solubility as well as different precipitation rate.

- It is not having universal experiment condition for the synthesis of various types of metal oxides.

2.4. Characterization techniques

2.4.4. Fourier transform infrared spectroscopy (FTIR)

FTIR is a powerful technique for identifying the structural coordination (types of chemical bonds) in the substances such as solids, liquids and gases. It is based on the interaction of IR radiation with the substance and the nature of interaction, which reveal the properties of the substance. When infrared light is passed through a sample of organic compound, some frequencies are absorbed, while other frequencies are transmitted without being absorbed. The transitions involved in the infrared absorption are associated with the vibrational changes in the molecule. Different bonds / functional groups have different vibrational frequencies and hence the presence of these bonds in a molecule can be detected by identifying this characteristic frequency as an absorption band in the infrared spectrum. The plot between transmittance against frequency is called infrared spectrum. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum: $\sim 4000 \text{ cm}^{-1}$ to $\sim 200 \text{ cm}^{-1}$.

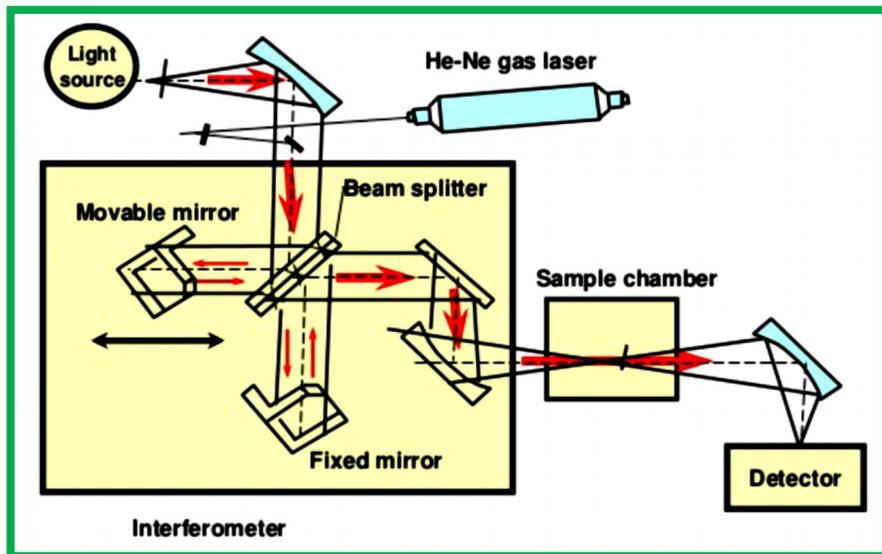


Fig. 2.2: Schematic diagram of FTIR

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy. There are three basic spectrometer components in an FT-IR system: radiation source, interferometer and detector. The IR radiation from a broadband source is first directed into an interferometer, where it is divided and then recombined after the split beams travel different optical paths to generate constructive and destructive interference. Next, the resulting beam passes through the sample compartment and reaches to the detector. Sample preparation is very easy. Almost any solid, liquid or gas sample can be analyzed. Fig. 2.2 shows the schematic diagram of FT-IR. The sample to be analyzed (minimum of 10 μg) should be ground into KBr matrix or dissolved in a suitable

solvent (CCl_4 and CS_2 are preferred). Water should be removed from sample if possible. In case of solid samples, it is mixed with solid KBr (transparent in the mid - IR region), then ground and pressed. The functional groups of Co_3O_4 nanoparticles were studied by FT-IR spectroscopy.

2.4.5. Raman Spectroscopy

Raman Spectroscopy is one of the vibrational spectroscopic techniques used to provide information on molecular vibrations and crystal structures. Raman spectroscopy is a method of determining modes of molecular vibrations. It is predominantly applicable to qualitative and quantitative analyses of covalently bonded molecules used to distinguish between different phases of the same material and can provide information on strain and periodicity in modulated structures. Raman signal occurs due to the change in polarizability of a molecule. This is a measure of the deformability of a bond in an electric field. The Raman effect is not an absorption effect like infrared, but depends on the polarizability of the vibrating group. Fig. 2.3 shows the principle of Raman spectroscopy.

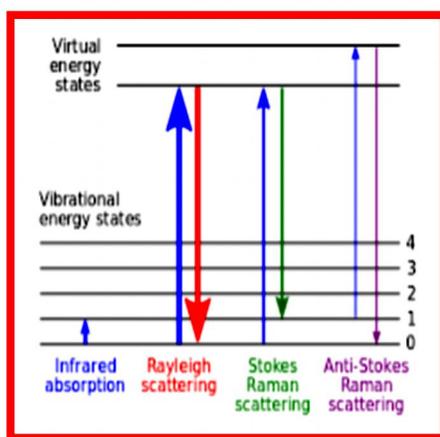


Fig. 2.3: Principle of Raman spectroscopy

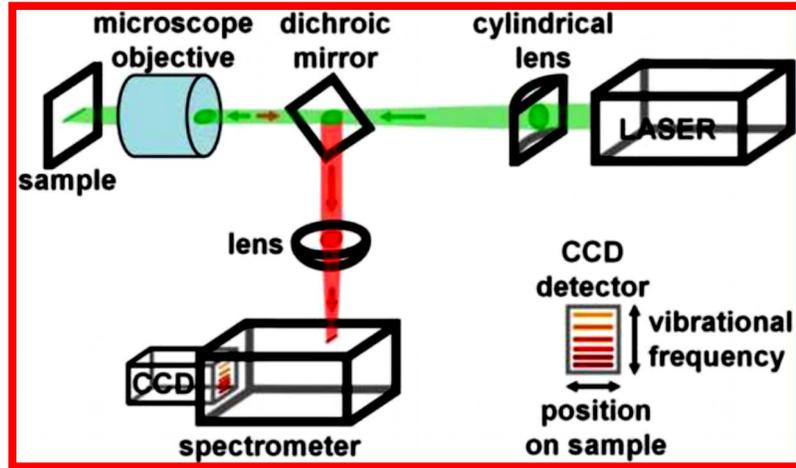


Fig. 2.4: Schematic diagram of Raman spectroscopy

A Raman system typically consists of four major components: excitation source (Laser), sample illumination system and light collection optics, wavelength selector (filter or spectrophotometer), detector (photodiode array, CCD or PMT). The sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through interference filter or spectrophotometer to obtain Raman spectrum of a sample. Fig. 2.4 shows the schematic diagram of Raman spectroscopy. Raman spectra are obtained from bulk solids, liquids, tablets, polymers, paper, etc. Sample preparations, such as grinding can also lead to changes in solid states (e.g. hydration state, polymorphism, hydrogen bonding), which sometimes have an impact on the final detection method. The Raman spectrometer was used to study the vibrational property of Co_3O_4 nanoparticles.

PREPARATION OF Co_3O_4 NANOPARTICLES BY CO-PRECIPIATION METHOD AND THEIR RESULTS

3.1. Introduction

Nanostructured materials have been widely investigated for the fundamental scientific and technological interests in accessing new classes of fundamental materials with unprecedented properties and applications. Inorganic nanomaterials have more attention because of the vast application as electrical, optical and magnetic properties [5]. In nanosized co-particles display a wide range of interesting size-dependent catalytic properties. In particular, because of their large surface area, co-nanoparticles showed high chemical reactivity which makes them suitable for catalysis. Co_3O_4 nanopowder which is p-type semiconductor and widely used in many fields such as magnetic, gas sensor, catalysis and electrochemical based on size, structure, shape, phase and surface morphology. Cobalt oxide plays an efficient role in memory storage [4].

3.2. Preparation of Co_3O_4 nanoparticles

Cobalt acetate is a moderately water soluble crystalline cobalt source that decomposes to cobalt oxide on heating. It is generally immediately available in most volumes. All metallic acetates are inorganic salts containing a metal cation and the acetate anion. Acetates are excellent precursors for the production of ultra high purity compounds, catalysts and nanoscale material. Oxalic acid is an organic compound with the formula $\text{C}_2\text{H}_2\text{O}_4$. It is a colorless crystalline solid that forms a colorless solution in DI water. It is used as an analytical reagent and general reducing agent.

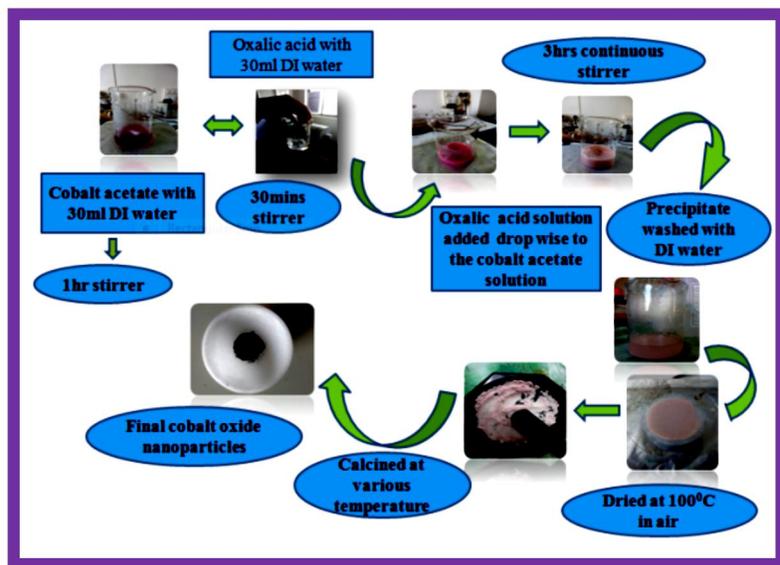


Fig. 3.1: Schematic representation of preparation method

The schematic representation of synthesis process is shown in Fig. 3.1. Cobalt acetate (0.3 M) solution was prepared by double distilled water (30 ml) and continuous stirring for 1 hr. Aqueous oxalic acid (0.3 M) solution was drop wise added to the cobalt acetate solution with continuous stirring for three hours. The resultant light pink coloured precipitates thus obtained were washed with double distilled water and then dried at 100 °C for 4 hrs. The synthesized powder was calcinated at various temperatures such as 200 °C, 300 °C, and 400 °C. Finally, black color Co_3O_4 nanoparticles were obtained.

3.3. Results and discussion

3.3.1. Fourier transform infrared spectroscopy

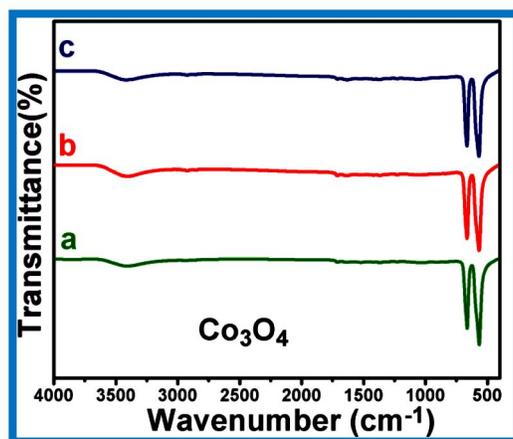


Fig.3.2: FT-IR spectra of Co₃O₄ nanoparticles calcinated at various temperatures (a) 200° C, 300° C and (c) 400° C

The chemical bonding information of the Co₃O₄ nanoparticles was studied using Fourier transform infrared spectroscopy (FT-IR) and the characteristics of IR bands are plotted in range of 4000-500 cm⁻¹ as shown in Fig 3.2. FT-IR spectroscopy was carried out in order to ascertain the purity and nature of metal or metal oxide nanoparticles. FT-IR spectra of Co₃O₄ nanoparticles showed significant absorption peaks at 567 and 661 cm⁻¹ are attributable to the fingerprint stretching vibrational modes of cobalt-oxygen (Co-O) bonds and thus confirms the formation of Co₃O₄ nanoparticles. The absorption band at 567 cm⁻¹ was assigned to Co-O stretching vibration mode which represents the presence of Co³⁺ ions in the octahedral site and 661 cm⁻¹ was assigned to the bridging vibration of O-Co-O bond denotes the Co²⁺Co³⁺O₃ bonding vibrations as in type ABO₃ (where A denotes the Co²⁺ in the tetrahedral site) of the crystal lattice structure[7]. The small broad band at 3440 cm⁻¹ is due to O-H stretching vibration modes for the adsorbed water molecules. The less intense band at 1635 cm⁻¹ is assigned to the bending mode of water molecule vibration. Increasing the calcination temperature reduces the intensity of the 3440 cm⁻¹, which may be due to the reduction in water content of the samples. No bands corresponding to acetate ions appear, indicating the complete removal of these ions through the preparation method [6].

3.3.2. Vibrational property

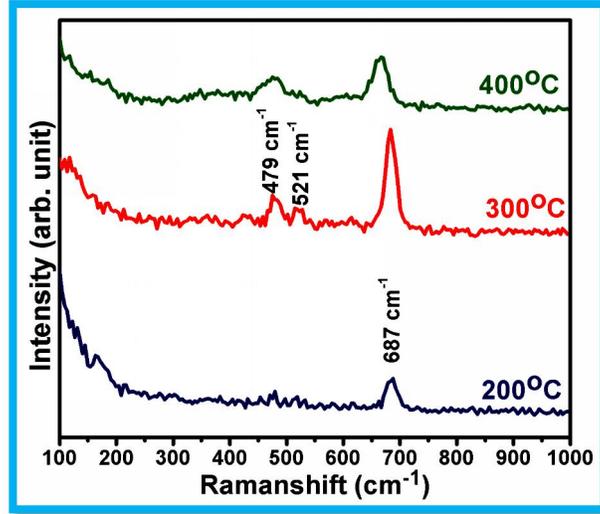


Fig.3.3:Raman spectra of Co₃O₄ nanoparticles calcinated at 200° C, 300° C and 400° C

Raman scattering is very sensitive to the microstructure of nanocrystalline materials, it is also used here to clarify the structure of the Co₃O₄ nanoparticles. For additional validation for vibrational frequencies, Raman spectrum was measured for the synthesized Co₃O₄ nanoparticles which are in the space group “Fd3m”. The active modes of Fd3m are given as follows:

$$\Gamma = A_{1g}(R) + E_g(R) + F_{1g}(1N) + 3F_{2g}(R) + 2A_{2u}(1N) + 2E_u(1N) + 4F_{1u}(1R) + 2F_{2u}(1N)$$

where (R), (IR), (IN) are depicted as Raman active, infrared active and inactive modes of vibrations [6]. Fig. 3.3 shows the Raman spectra of Co₃O₄ nanoparticles prepared with various calcination temperatures. As shown in the Fig. 3.6, the Raman spectra of Co₃O₄ nanoparticles show three obvious peaks located at around 479 cm⁻¹, 521 cm⁻¹ and 687 cm⁻¹ corresponding to the three Raman active modes of Co₃O₄. The Raman band with medium intensity located at 479 cm⁻¹ is assigned to E_g mode and the centered weak intensity is located at 521 cm⁻¹ is assigned to 3F_{2g} mode and the strong intensity located at 687 cm⁻¹ is assigned to A_{1g} mode. The Raman shifts are consistent with those of pure crystalline Co₃O₄, indicating that the Co₃O₄ nanoparticles have

a similar crystal structure of the bulk Co_3O_4 . However, compared with that for bulk Co_3O_4 , the peak positions of the three active modes of E_g , F_{2g} , A_{1g} shift to low wavenumber about 15, 13, 16 cm^{-1} , respectively. This phenomenon is attributed to the optical phonon confinement effect in nanostructures that can cause uncertainty in the phonon wavevectors and then a downshift of the Raman peaks [7].

SUMMARY AND CONCLUSIONS

In summary, Co_3O_4 nanoparticles were successfully synthesized by co-precipitation method. The synthesized cobalt oxide nanoparticles were characterized by using FTIR and Raman studies. FT-IR analysis confirms the formation of the Co_3O_4 nanoparticles. FT-IR spectrum shows absorption band at 567 cm^{-1} for Co-O and 661 cm^{-1} for O-Co-O vibration modes. Raman spectra of Co_3O_4 nanoparticles show three peaks located at around 479 cm^{-1} , 521 cm^{-1} and 687 cm^{-1} corresponding to the three Raman active modes of Co_3O_4 [6]. In conclusion, the co-precipitation method is simple, low cost, safe and suitable for the production of high purity Co_3O_4 nanoparticles for various applications.

References

1. T. Pradeep, Nano: The essentials, ISBN-13:978-0-07-061788-9, (2009).
2. J. Kreuter, Int. J. Pharm., 331, pp:1-10, (2007).
3. Taylor and Francis, Handbook on Nanoscience, Engineering and Technology, 2nd edition.
4. Harish Kumar , Poonam Sangwan, Manisha, Advances in Applied Physical and Chemical Sciences-A Sustainable Approach - ISBN: 978-93-83083-72-5, pp: 99-103, (2017).

5. Dr. S.V. Jagtap, A.S. Tale, S.D. Thakre, International Journal of Research in Engineering and Applied Sciences(IJREAS), ISSN (O): 2249-3905, Vol. 7, pp: 1~6, (August-2017).

6. S. K. Jesudoss, J. Judith Vijaya, P. Iyyappa Rajan, K. Kaviyarasu, M. Sivachidambaram, L.John Kennedy, HamadA. Al-Lohedan and Jothiramalingam, Photo Chemical and Photobiological Science, March 2017 (Manuscript).

7. Harish Kumar , Poonam Sangwan, Manisha, Advances in Applied Physical and Chemical Sciences-A Sustainable Approach - ISBN: 978-93-83083-72-5, pp: 99-103, (2017).