OPTICAL PROPERTIES OF COBALT OXIDE NANOPARTICLES BY SOL-GEL METHOD

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Abstract

Co_3O_4 nanoparticles are used as p-type semiconductor. The Photoluminescence sharp peaks shows a near and edge emission located at UV region and green emissions. It is noted from the spectra that the intensity of UV emission is dominated than the visible emission related that the surface morphology.

Key Words: Cobalt Oxide Nanoparticles, PL, UV Analysis

1.1 Introduction

Nanotechnology can be defined as research and technology development at theatomic, 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 smallstructures. Nanotechnology, which is one of the novel technologies, discusses to the development of structures, devices and systems having size 1-100 nm [2].

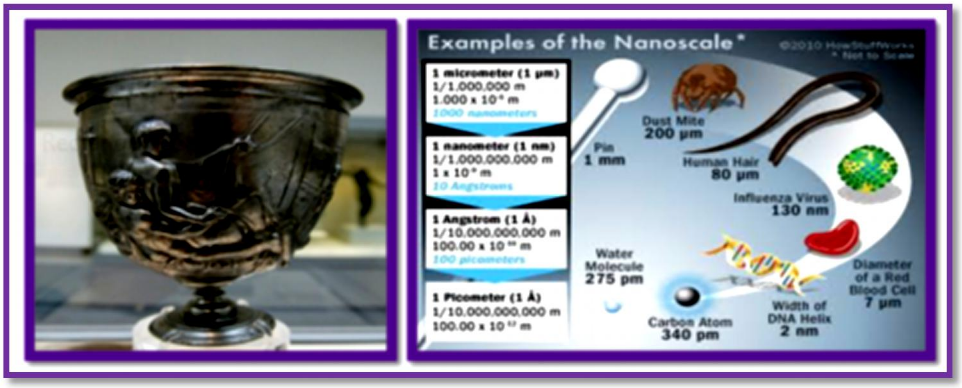

Fig. 1.1: Examples of nanotechnology and nanoscale materials

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.

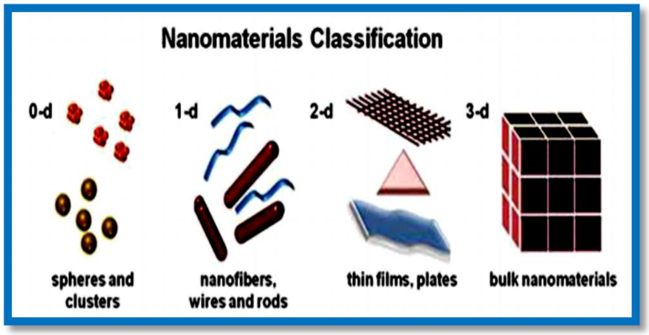

Fig. 1.2: Classification of nanomaterials under dimensions

Two dimensional: This type of nanomaterials also outside the nanometer range. Theseinclude 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 composedof the individual blocks which are in the nanometer scale.

1.2.2. On the basis of structural configuration

Carbon basednanomaterials: The nature of this kindof 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].

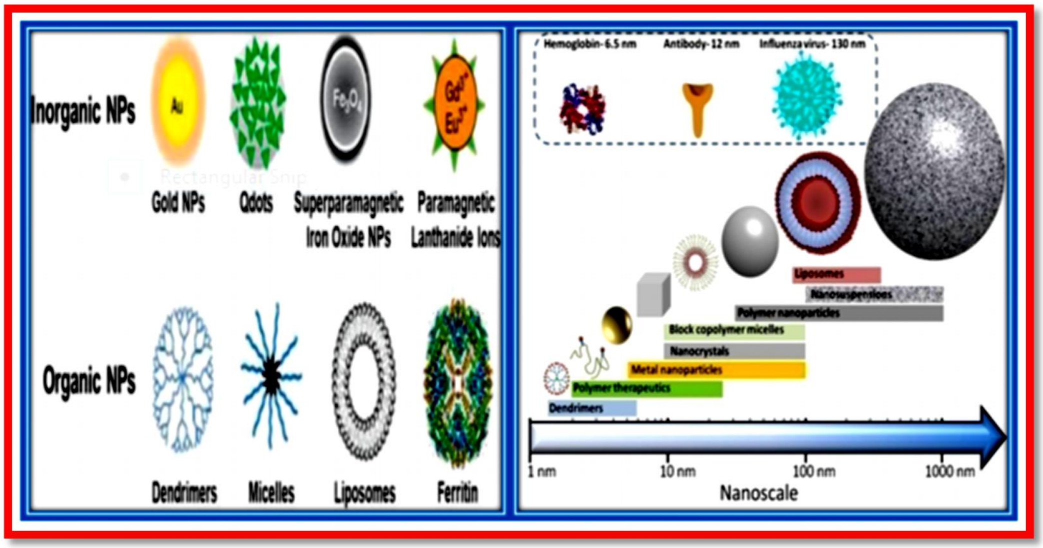

Fig. 1.3: Classification of nanomaterial under structural configuration

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 mechanicalstrength 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 transfort 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 valance 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 $Co^{II}Co_2{}^{III}O_4$ and sometimes as $CoO.Co_2O_3$. 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].

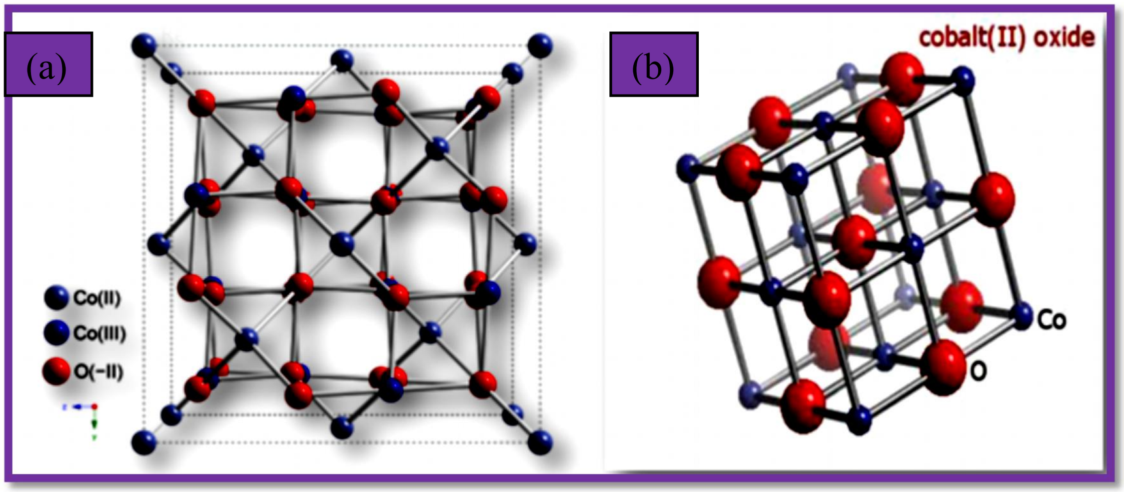

Fig. 1.4: (a) Cobalt (II, III) oxide structure, (b) Cobalt (II) oxide structure

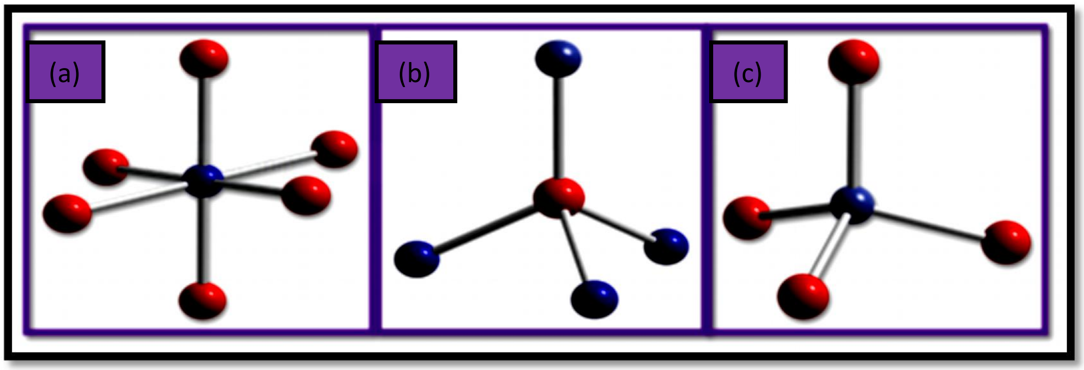

Fig. 1.5: a) Tetrahedral co-ordination geometry of Co(II), b) Distorted octahedral co-ordination geometry of Co(III) and c) Distorted tetrahedral co-ordination geometry of O

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 locks fit together to producer 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.

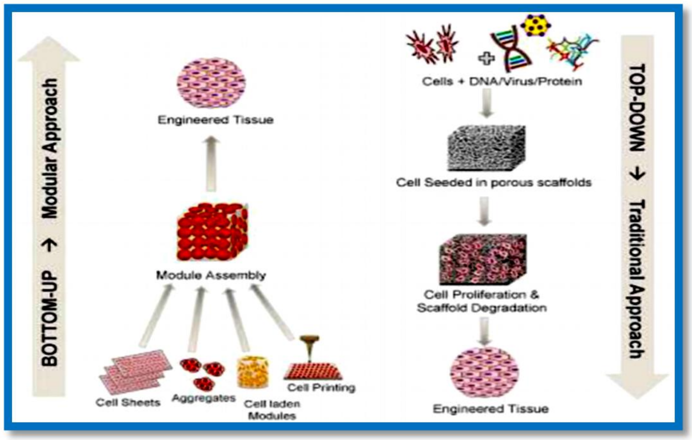

Fig. 2.1: Two approaches of synthesis of nanoparticles

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.

CHAPTER – III

PREPARATION OF Co_3O_4 NANOPARTICLES BY CO-PRECIPITATION METHOD AND THER 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 $C_2H_2O_4$. 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.

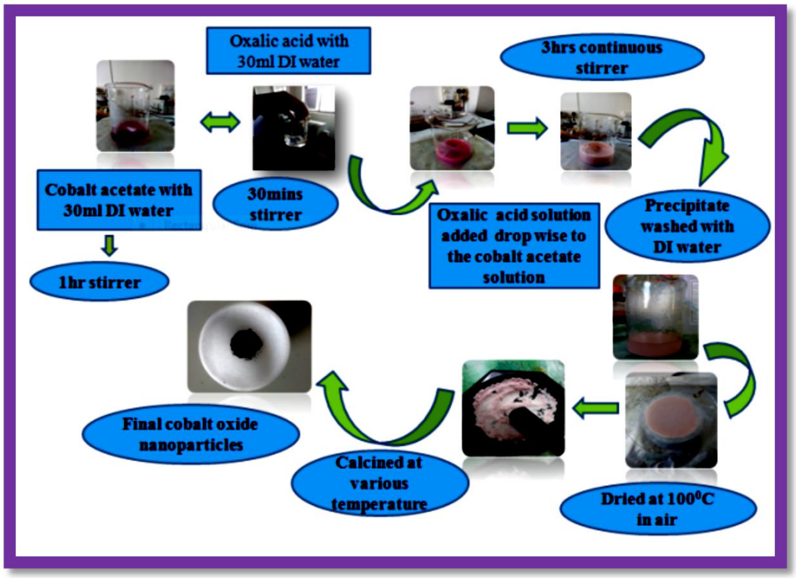

Fig. 3.1: Schematic representation of preparation method

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

3.3.2. UV-Visible spectrophotometer result

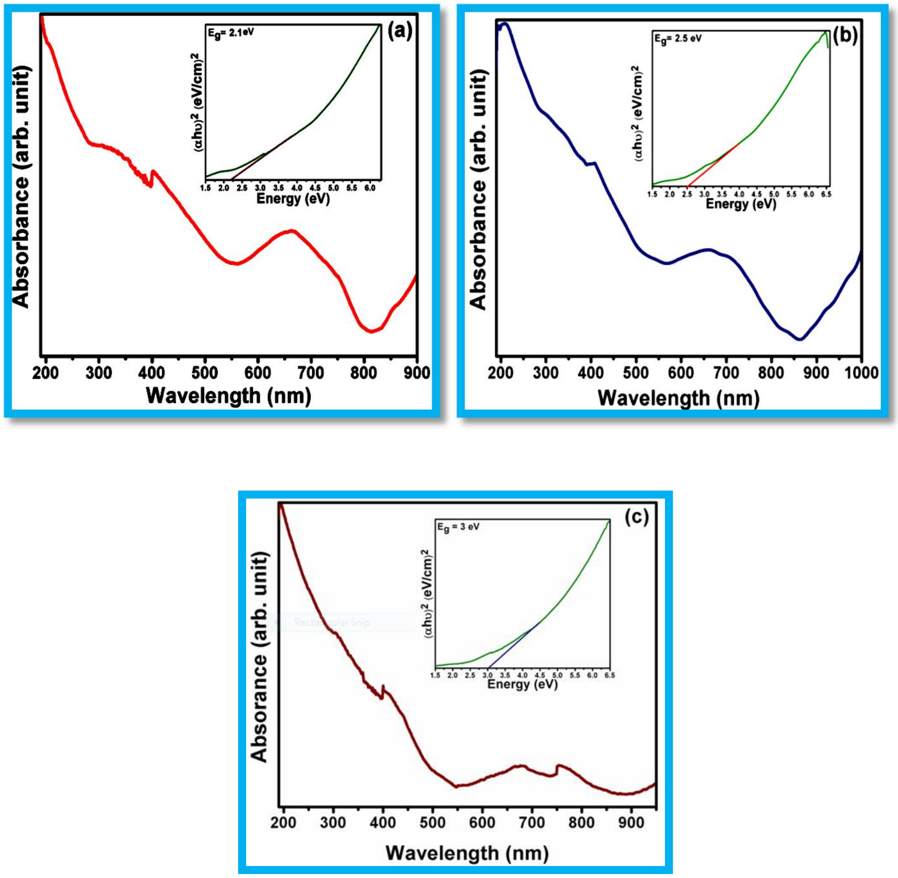

Fig. 3.2: Optical absorbance spectra of calcinated Co_3O_4 nanoparticles at (a) 200 ° C, (b) 300°C and (c) 400°C. Insets show the Tauc plots.

The optical absorption spectra of the Co_3O_4 nanoparticles were carried out using UV-vis spectrophotometer. Fig. 3.2 shows the absorption spectra of synthesized nanoparticles at various calcinated temperatures. The optical absorption shows two peaks in the visible region, which can be assigned to the $O^{2-} \rightarrow Co^{2+}$ and $O^{2-} \rightarrow Co^{3+}$ charge transfer processes [5].

The optical energy band gap of Co_3O_4 nanoparticles were estimated from absorption coefficient (α) and photon energy (hν) using the Tauc's relation

$$(\alpha h\nu) = A(h\nu - E)^n$$

where, α is the absorption coefficient, hν is the incident photon energy, A is constant and the value of n is 2 for a direct transition and 1/2 for an indirect transition. In this case, n = 2 for the determination of optical direct band gap of Co_3O_4 nanoparticles. Insets of Fig. 3.2 shows the plots of $(\alpha h\nu)^2$ versus photon energy (hν). The band gap values of Co_3O_4 nanoparticles were calculated as 2.1 eV (590 nm), 2.5 eV (495 nm) and 3 eV(413 nm) usingTauc's relation for the samples calcinated at 200˚C, 300°C and 400˚C, respectively. This energy band gaps are greater than those of bulk Co_3O_4. The increase in the band gaps can be related to the quantum confinement effects of Co_3O_4 nanoparticles [6].

3.3.3. Photoluminescence study

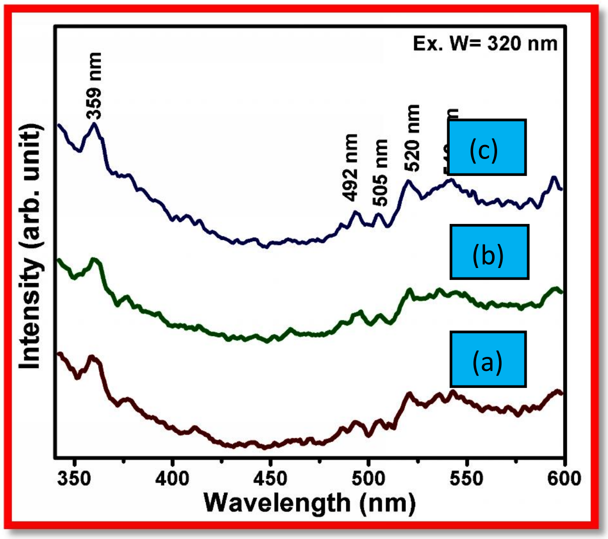

Fig. 3.3: PL emission spectra of Co_3O_4 nanoparticlescalcinated at (a) 200° C, (b) 300° C and (c) 400° C

The photoluminescence emission spectrum can provide valuable information about the intrinsic and extrinsic defects in the crystals lattice of nanoparticles.Fig. 3.3. shows the room temperature PL emission spectra of Co_3O_4nanoparticles calcinated at various temperatures.The samples were excited with an excitation wavelength of 320 nm. It is well known that the optical properties of Co_3O_4 nanoparticles are closely dependent on their structures and morphologies. In metal oxide nanostructures, the PL emission is usually classified into two sections including near band edge (NBE), UV emission and deep level (DL) defectassociatedto the visible emission. The UV emission is commonly attributed to the direct recombination of the excitons through an exciton-exciton scattering. The visible emission originates from the radiative recombination of a photo-generated hole caused by the impurities and structural defects in the crystal, for instance, oxygen vacancies and cobalt interstitials. In general, the emission spectrum of the Co_3O_4 sample may have emission bands at 200-380 nm and 400-580nm wavelength ranges. The broad peak exhibited at 359 nm (3.5 eV) in UV region is due to the impact of calcination temperatures (200˚C, 300°C and 400˚C). The set of peaks observed at 492 nm (2.5 eV) and 520 nm (2.4 eV) were belongs to green emission. It is noted from the spectra that the intensity of UV emission is dominated than the visible emission, related that the surface morphology plays an important role for the determination of optical properties [7].

SUMMARY AND CONCLUSIONS

In the summary of present work, Co_3O_4 nanoparticles were successfully achieved by sol-gel method. The synthesized cobalt oxide nanoparticles were characterized by using UV-visible, PL studies. The optical energy band gap values estimated by UV-visible analysisreported that the energy band gap values areincreased with increase in calcination temperature. So that Co_3O_4 nanoparticles are used as p-type semiconductor. The Photoluminescence sharp peaks shows a near and edge emission located at UV region and green emissions. It is noted from the spectra that the intensity of UV emission is dominated than the visible emission related that the surface morphology plays an important role for the determination of optical properties. This method is simple, low cost, safe and suitable for the industrial production of high purity Co_3O_4 nanoparticles for various applications.

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