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Synthesis and Characterization of Nano sized Cobalt Oxide by Precipitation Method

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Abstract

In the present work, cobalt oxide nanoparticles were prepared by using precipitation method. The cobalt nitrate [$Co(No_3)_2$] and ammonium oxalate [C_2H_8 N_2O_4] were used as precursors for the synthesis of cobalt oxide nanoparticles and the resultant product was Calcinated at 400°C for 2 hrs. The synthesized nanoparticles were characterized by X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Election Microscope (SEM). Energy Dispersive X ray Spectroscopy (EDAX) to analyze the structural and morphological properties. The XRD pattern of the synthesized cobalt oxide nanoparticles exhibits cubic structure with the average crystalline size of 8.06 inn. The functional groups of the synthesized nanoparticles were confirmed by using FTIR spectrum (400 to 4000 cm^1). In the synthesized sample and its purity were confirmed from EDAX spectrum The surface morphology of the synthesized Co_3O_4 nanoparticles shows spherical morphology. The optical properties of the synthesized cobalt oxide nanoparticles were investigated by photoluminescence spectrum which shows a minor emission at around 440 mil.

Keywords: Cobalt Oxide. Precipitation. XRD. FTIR. SEM. EDAX and Photoluminescence.

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1. Introduction

Nanotechnology is the study of controlling matter on an atomic and molecular scale. Generally, Nanotechnology deals with structures sized between 1 to 100 nanometers. Nanotechnology is a modern multidisciplinary science involving the fields of physics, biology, chemistry and Engineering. Because of the particular properties of nanoparticles in comparison with the bulk materials, recently many researchers focus on transition metal oxides. Among various oxides, Co_3O_4 is an interesting material belonging to the normal spinel ciystal structure $A_8B_{16}O_{32}$ in which Co (II) ions occupy the tetrahedral 8a sites and Co (III) ions occupy the octahedral 16d sites.[1-2] Cobalt Oxide is an inorganic compound with melting point in the order of 895 °C and boiling point is in the order of 900°C. Co_3O_4 is a black antiferromagnetic solid.[3] Co_3O_4 nanoparticles appear as a white powder and it is an important magnetic material. Co_3O_4 P-type metal oxide semiconductor and furthermost it has stable phase in the Co-0 system.[4-5] Co_3O_4 NP's can be synthesized by various methods like hydrosolvothermal method , combustion method , sol-gel process, microwave heating method,[6] spray pyrolysis and polyol method.[7] Depending on the synthetic route, cobalt nanoparticles has three different types named as Co-hcp, e-Co cubic and FCC structures.[8] In the field of Microelectronics magnetic nanoparticles has variety of applications such as, micro batteries,[9] nanowires,[13] specific alloy[10] and catalytic applications.[11] Co_3O_4 nanoparticles can act as a catalyst for different organic pollutants and plays an important role as a photo catalyst agent for the degradation of methylene blue dye.[12] Co_3O_4 nanoparticles are widely used in technical applications such as electrochemistry, sensors, magnetic fluids, energy storage devices and biomedicine.[13,14] It is a very important ingredient for the wide range of application in solid state sensors, Electrochromic devices, heterogeneous catalyst, lithium ion batteries and solar energy absorbers is due to its fascinating properties and temperature stability. Co_3O_4 nanoparticles can also be used as an electrode material for super capacitors. The PL spectrum provides the transition energies, which can be used

to determine electronic energy levels. The PL intensity gives a measure of the relative rates of radiative and non radiative recombination. Variation of the PL intensity with external parameters like temperature and applied voltage can be used to characterize further underlying electronic states and bands. PL is used to study any surface, virtually in any environment and also it is used to monitor changes induced by surface modification in real time. For example, unlike most surface characterization techniques, PL is generally not sensitive to the pressure of the sample chamber. Hence, it is used to study surface properties in relatively high-pressure semiconductor growth reactors.[15-21] Photoluminescence properties exhibited by the various nano materials like Fe_2O_3 , $S_{11}O_2$ and TiCh were reported by R.K. Mishra *et al.*,[22] and Brahim Dkhil *et al*.[23] In the present work, the photoluminescence property of the Co_3O_4 synthesized using simple and cost effective precipitation method at low temperature[5-8] was investigated.

2. Experimental Procedure

In this present work, Co_3O_4 nanoparticles were prepared by precipitation method using cobalt nitrate, ammonium oxalate as a starting precursor. In this process, 0.5 M concentration of cobalt nitrate were dissolved in 20 ml of distilled water and stirred continuously using a magnetic stirrer to get a clear pink colour solution. Then 0.5 M of ammonium oxalate solution was stirred separately until a clear homogeneous solution was obtained and the ammonium oxalate solution was added drop by drop to cobalt nitrate solution under constant stirring till colour of the solution changes from pink to purple. In the final complex mixture, purple colour precipitate was settled at the bottom of the beaker. The precipitate was washed thoroughly with the help of double distilled water for three times followed by ethanol wash. The resulting precipitate was kept in hot air oven at 100°C for 2 hrs for complete drying. Then the obtained Co_3O_4 nanoparticles were calcinated in muffle furnace for 2 hrs at 400°C and ground well with agate mortar. A black colour Co_3O_4 powder obtained was collected carefully and stored in an air tight container for further usage. Fig. 1 shows the schematic and visual observation of preparation Co_3O_4 nanoparticles.

2.1 Characterization Techniques

The crystal structure of the annealed sample was analyzed using X-ray pattern, obtained by bruker diffractometer with Cuk as an X-ray source. The FTIR spectrum was recorded using Perkin-Elmer system 2000. SEM with EDAX was carried out using Philips xl-30 to analyze the surface morphology and elemental composition of the prepared cobalt Oxide nanoparticles. The optical studies were carried out using photolurninescence spectra recorded using UV-Vis-Nir spectrophotometer (Jasco).

3. Results and Discussions

3.1 XRD Analysis

The X-ray powder diffraction pattern of the synthesized cobalt oxide nanoparticles by precipitation method was carried out to analyze the crystallographic properties. The XRD plot of the synthesized sample (Fig. 2) exhibits the major diffraction peaks at 18.9 , 36.6 and 65.0 assigned to diffraction planes (111), (311) and (440) respectively[14] as it does not contain any characteristics peaks other than Co_3O_4 peaks which indicates that the synthesized Co_3O_4 nanoparticles

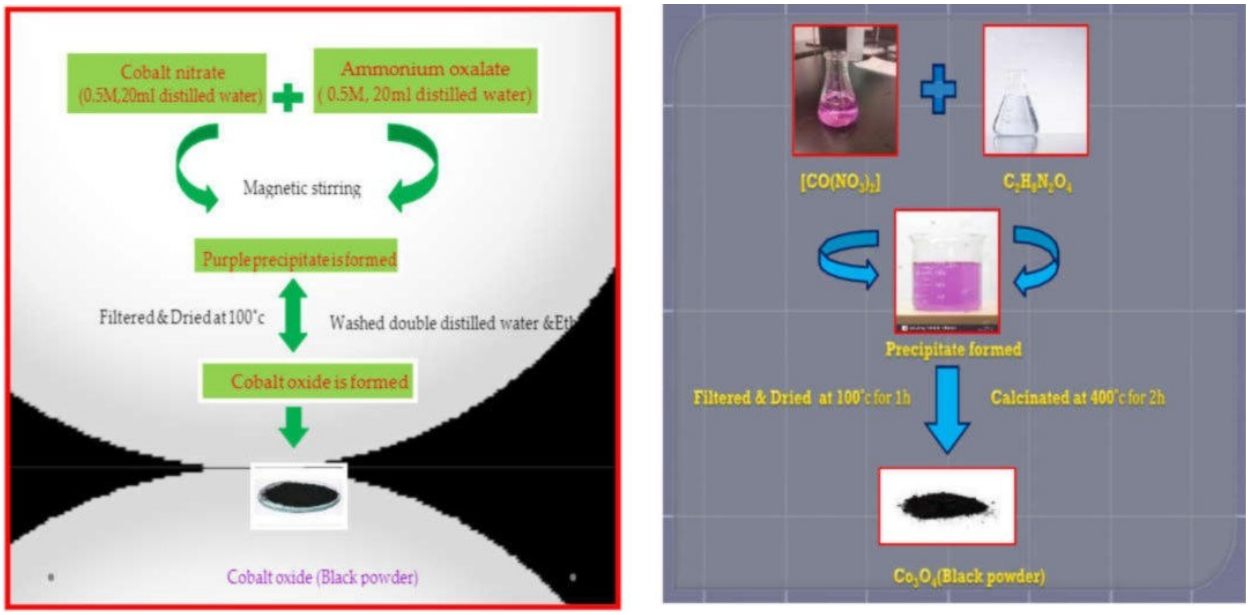

Fig. 1: Schematic Representation and Visual Representation of synthesis of Co_3O_4 nanoparticles

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were free of impurities. Crystallite size of the prepared cobalt nanoparticles was calculated using Debye's Scherer formula and the values of the structural parameters were tabulated in Table 1.

The Debye's Scherer formula is given by the equation (1)

$$D = k\lambda / \beta\cos\theta \quad (1)$$

Micro Strain

The micro strain can be calculated from the following equation (2)

$$XIO^{-3} \quad (2)$$

Where,

= full with half maximum of the peak in radians

θ= diffracted angle of X-ray pattern in degrees

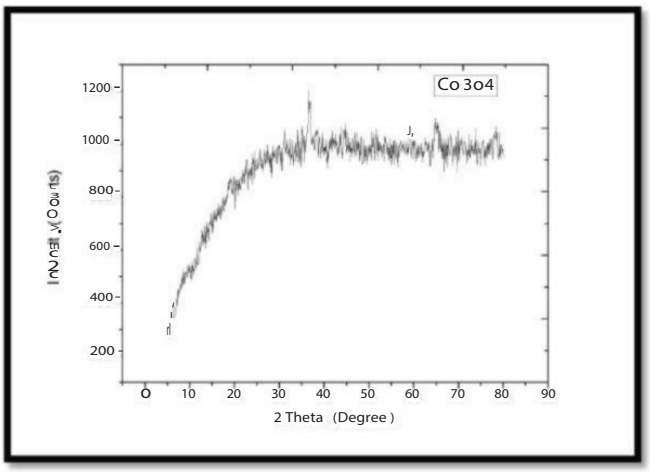

Fig. 2: XRD image for Cobalt Oxide nanoparticles

Dislocation Density

The dislocation density can be calculated

$$A = 1/D^2 \quad (3)$$

Where,

D= crystallite size of the sample in nm

Lattice Parameter

The lattice parameter can be calculated using Bragg's law and Interplaner spacing[21]

Where,

$$A = 8.05Å$$

The Lattice parameter constant (for 2θ=36.6619 deg) can be estimated using above formula (a=b=c=8.05Å), which are consistent with those reported in ICPDS card No. 76-1802.[20]

3.2 SEM Analysis

The structural morphology of the synthesized Co_3O_4 nanoparticles was examined using scanning electron microscope (SEM). Fig. 3 shows the SEM images of Co_3O_4 nanoparticles at different resolution. The surface morphology of prepared Co_3O_4 shows uniform distribution of spherical structure without any indistinguishable particles. However, a close investigation reveals that a number of fine particles clings together to form a spherical particle of bigger particle size. SEM images show clear images of the structure variation among low and high magnification (10 kv - 30 kv).

3.3 EDAX analysis

The elemental composition of the synthesized Co_3O_4 nanoparticles prepared by precipitation method was

Table 1: Structural analysis of Cobalt Oxide nanoparticles

2θ (deg)	FWHM (deg)	FWHM Rad (10^{-3})m	Crystalline Size D (10^{-9})m	Average Crystalline size D (10^{-9}) m	Micro Strain c (10^{-3})m	Dislocation density (10^{15}) m
36.6619	0.81540	14.22419	10.72544	8.060267	3.375578	0.086932

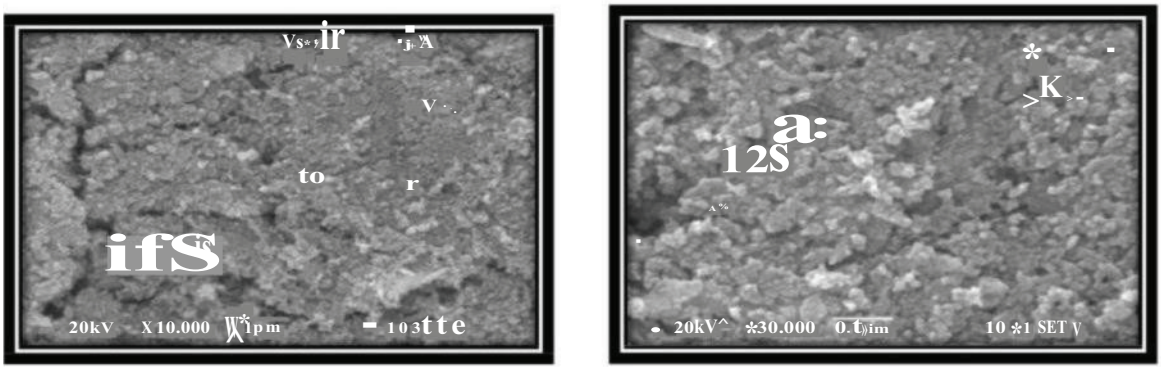

Fig. 3: SEM images of $Co3O_4$ nanoparticles

analyzed using Energy dispersive spectroscopy. EDAX spectrum Fig. 4 reveals the presence of cobalt and oxide by two strong peaks and indicates the absence of impurities. The formation of Co_3O_4 nanoparticles was confirmed with a weight percentage of 68.93% of cobalt and 31.07% of oxygen.

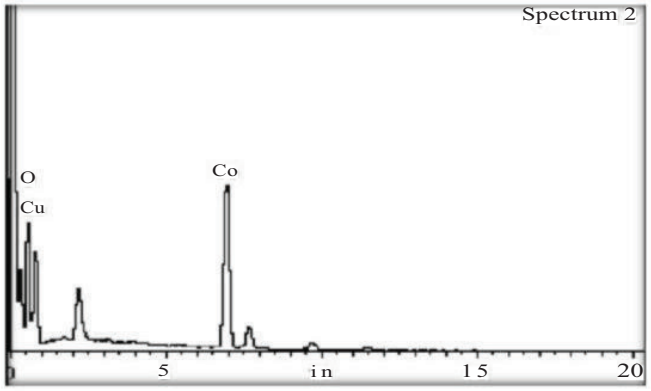

Fig. 4: EDAX spectrum Co3O4 nanoparticles

3.4 FTIR Analysis

FTIR spectroscopy was employed to identify functional groups present in the synthesized nanoparticles.

FTIR Spectrum of Co_3O_4 shows peak at 550 cm^{-1} which corresponds to the vibrations of Co^{3+} octahedral hole and peak at 667 cm^{-1} is attributed to stretching vibrations of Co^{2+} in tetrahedral hole.[15-19] The absorption band at 3429.43 cm^{-1} indicates the stretching mode vibration of alcohol (O-H) group. The transmittance of Co_3O_4 nanoparticles recorded in the range 400 to 4000 cm^{-1} was shown Fig. 5 in graph.

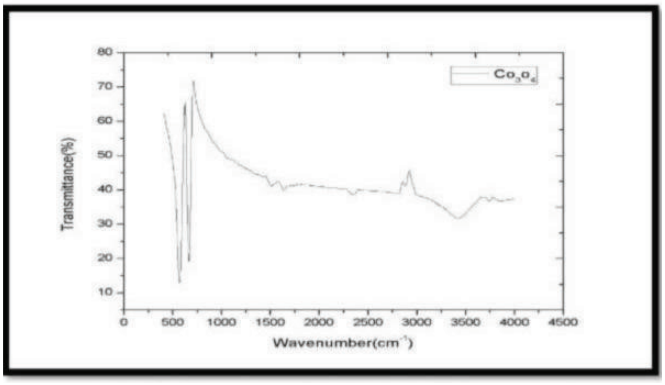

Fig. 5: FTIR spectrum of Cobalt Oxide Nanoparticles

3.5 Photoluminescence

PL emission spectrum of Co_3O_4 nanoparticles was investigated using Florescence spectrophotometer[16] The PL spectrum exhibits an emission band spreading from 400 to 500 nm. A slightly broad blue emission peak was observed at 440 nm (Fig. 6).

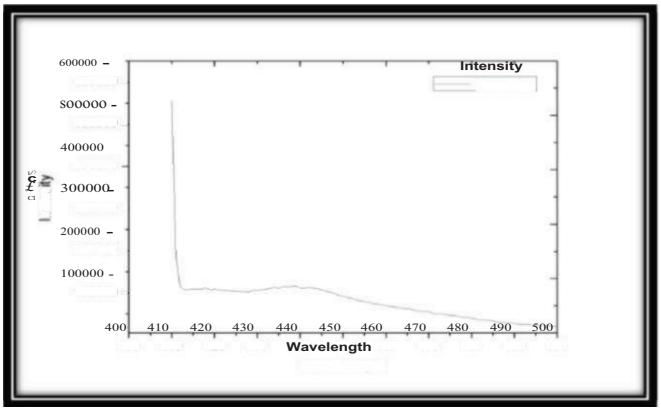

Fig. 6: PL spectrum of Co_3O_4 nanoparticles

4. Conclusion

In the present work, Co_3O_4 nanoparticles were successfully achieved by Precipitation method. The straight line and peak in XRD pattern reveals that the synthesized cobalt nanoparticles were polycrystalline in nature. The average particle size of cobalt oxide nanoparticles was found to be 8.06 nm. The spherical structure was observed from SEM image of Co_3O_4 Nanoparticles. EDAX spectrum displays the elemental conformation of Co_3O_4 nanoparticles by the presence of Co and 0. The stretching mode of Co-0 bond of the Co_3O_4 was confirmed by FTIR spectrum. PL Spectrum shows the emission peak in the visible region.

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