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Study on Cobalt Ferrite Nanoparticles Synthesized by Co-Precipitation Technique for Photo-Fenton Application

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Keywords: inverse spinel cobalt ferrite (CoFe₂O₄), nanomaterials, co-precipitation method, optical properties, weak ferromagnetic nature.

ABSTRACT. Inverse spinel Cobalt ferrite (CoFe₂O₄) nanoparticles has fascinated colossal attention owing to its remarkable photo fenton activity and extra ordinary amalgamation of its properties specially its optical and magnetic properties are catered as suitable candidates in the field of electronics. Their high electrical resistivity prevents induction of eddy currents and the resultant loss of energy. Ferrites are economically viable and their magnetic and optical properties can be tailored as per the requirement of applications. Nanostructured cobalt ferrite particles were synthesised using scalable and facile co-precipitation technique by maintaining pH 9 by using the precursor solution. The particle size, morphology and reaction rate of the nanoparticles could be well tailored. The prepared CoFe₂O₄ nanoparticles were characterized by X-ray diffraction (XRD) reveals the crystalline nature of the synthesized product, PL photoluminescence spectra and UV-Vis Spectroscopy (UV-Vis) divulges the optical properties and the spectrum is further used to evaluate the optical constants required for fabrication and Using, VSM, the magnetic behavior of the material have been determined. Degradation of Methylene blue dye using synthesized sample was studied for photocatalytic application.

Introduction. Over last few years, nano sized materials have been extensively studied worldwide, owing to its pro and unique applications to communal at large and to have a deeper perceptive on the exceptional and challenging behavior of materials, hence nanotechnology field is zealously hunted by the researcher community. The inimitable attribute of nanomaterials arises, due to their inimitable physical properties like electrical conductivity, refractive index, optical band gap, magnetic properties and superior mechanical properties such as stringency of the nano sized material are being revealed and inferred progressively by the techno crafts and scientists.

Among diverse nanomaterials, inverse spinel ferrite nanoparticles have become incalculably popular for a spacious variety of applications [1], such as photocatalytic activity, magnetic resonance imaging contrast enhancement, hot gas desulphurization, magnetic refrigerator, superconductors, gas-sensitive materials, flexible recording media, Li-batteries etc. Among spinel ferrites, cobalt ferrite has been the area of concern due to its unique properties such as thermal stability and chemical the particle size dependence of magnetic properties. The dispersion routes to synthesize CoFe₂O₄ are many such as microemulsion method, co-precipitation, sol-gel, ball milling, ceramic method, hydrothermal method and solvothermal synthesis etc, [2-4]. Among these, co-precipitation is an uncomplicated and economically viable technique to prepare inverse spinel structured ferrite nanoparticles at low temperatures. In this work, we have synthesized cobalt ferrite nanoparticles via the co-precipitation technique to investigate their structural, optical, magnetic property and their degradation efficiency.
Experimental. Cobalt Nitrate (Co(NO₃)₂) and ferric Nitrate (Fe(NO₃)₃) of analytically graded Merck chemical were used without further purification. Initially Co(NO₃)₂ (0.1 M) and Fe(NO₃)₃ (0.2 M) were dissolved in 100 mL of distilled water separately and stirred in order to obtain a lucid solution. Then mineralizer (NaOH) was added drop wise in line to achieve pH 9 under continuous stirring, finally the obtained by precipitate was stirred at 80 °C for 3h. As a result, brown precipitate was centrifuged thrice with double distilled water and twice with ethanol. The obtained product was dried at 80 °C for 24 hours in an oven, followed by calcination at 500 °C to a further period of 5 hours to obtain the final product of CoFe₂O₄ nanoparticles. The sample thus obtained was characterized.

Results and discussion. Crystalline nature and phase formation of the CoFe₂O₄ powder were notorious by recording their X-ray diffractograms using Bruker AXS D8 Advance instrument with Cu Kα radiation (λ=1.540598 Å) in the 2θ range 20 - 70° is shown in Fig. 1. It was confined that all the peaks of CoFe₂O₄ matches well with the JCPDS No.22-1086. Hence the observed patterns have been clearly endorsed to the presence of spinel structure. The particle size of the co-precipitated products strongly depends on the precipitation medium and molarity of the precursor. The crystallite size was calculated by using the Scherrer formula [5],

\[ \Phi = \frac{k\lambda}{\beta \cos \theta} \]  

![Fig. 1. XRD pattern of CoFe₂O₄ nanoparticle.](image)

The crystallite size was found to be around 16 nm. The FTIR spectra recorded the information about the positions occupied by the ions is shown in Fig. 2. The wide band in the region of 3403 cm⁻¹ corresponds to OH group of CoFe₂O₄ nanoparticles. The peaks at 549 and 451 cm⁻¹ are owed to stretching vibration of M-O bond in octahedral and tetrahedral sites were 451 cm⁻¹ is assigned to be Co-O band and 549 cm⁻¹ is associated to Fe-O band. The band observed around 1379 and 3403 cm⁻¹ frequency are endorsed due to the stretching of H-O-H binding. The particle size and morphology of the cobalt ferrite nanoparticles was investigated by High Resolution Transmission Electron microscope (HRTEM) model Joel/TEM 2100. The arbitrary direction of particles allows for a geometrical measure of the size distribution shown in Fig. 3. The pH had no noticeable sway on the morphology, but it affects the crystalline size, which demonstrates that the CoFe₂O₄ nanoparticles are cubically spherical with an average grain size of about 9 nm, which is smaller than Scherrer calculation.
Fig. 2. FTIR of CoFe$_2$O$_4$ nanoparticles.

Fig. 3. HR-TEM of CoFe$_2$O$_4$ nanoparticle Ultraviolet-visible spectroscopy refers to reflectance spectroscopy or absorption spectroscopy in the visible spectral region (i.e. 200 – 800 nm).

Fig. 4 Optical absorption spectra of CoFe$_2$O$_4$. 
In this vastness of the electromagnetic spectrum, ions, atoms or molecules undergo electronic transitions from the ground to excited state. UV–vis spectra (Fig.4) for CoFe$_2$O$_4$ sample are recorded in the range 200–800 nm. The absorbance result demonstrated that CoFe$_2$O$_4$ nanoparticles had considerable absorbance in the range of 542 nm wavelength. The band gap energy was estimated from the intercept of $hv$ vs $(ahv)^2$ for direct transitions as shown in Fig. 4. The optical absorption coefficient is calculated by the equation,

$$ahv = A (hv - Eg)^{1/2}$$  \hspace{1cm} (2)

where $h$, $\alpha$, $\nu$, $Eg$ and $A$ are the Planck constant, light frequency, absorption coefficient, band gap and proportionality constant.

The band gap value was 2.14 eV, the red shift to bulk band gap. The band gap value is influenced by various factors such as presence of impurities, crystalline size and structural parameters [6]. From the emission spectrum shown in Fig.5, a broad visible emission is being harnessed in the intact PL spectrum, which has been assigned due to the charge convey between Zn$^{2+}$ at tetrahedral sites and Fe$^{3+}$ at octahedral sites which is bounded by O$^{2-}$ ions. The excitation wavelength is at 418 nm for CoFe$_2$O$_4$, which trait to the recombination of holes and electrons in the valence and conduction band [7].

![Fig. 5. PL spectra of CoFe$_2$O$_4$](image1)

![Fig. 6. Magnetization curve for CoFe$_2$O$_4$.](image2)

The magnetic properties of CoFe$_2$O$_4$ particles were pragmatic using a vibrating sample magnetometer (VSM) Lakeshore VSM 7407 with magnetic field 2.5 T at room temperature (303 K). In Fig. 6 hysteresis loops is extremely narrow for the reason that the particles is of small average diameter. The saturation magnetization ($M_s$) for synthesized sample was derived from the law of saturation using the following equation:

$$M = M_s \left(1 - \frac{A}{h} - \frac{B}{h^2}\right) + \chi_F H$$  \hspace{1cm} (3)

where $A$ is inhomogeneity parameter, $M_s$ is the saturation magnetization, $B$ is the anisotropy and $\chi_F$ is the highest field susceptibility parameter.

The loop indicates a steep ascends of magnetization as the applied field increases. The superior slope of the curve results to the abridged anisotropy. The coercivity ($H_c$), saturation magnetization ($M_s$) and
retentivity ($M_r$) values of the synthesized sample are 333.76 (emu/g), 0.5656 G and 0.10134 (emu/g) respectively. The squareness value of the hysteresis loop is found to be 0.179 (emu/g).

![Absorption Spectra](image)

**Fig. 7. Change in absorption spectra of MB with time in the presence of CoFe2O4 nanoparticles.**

The curve indicates the definite ordering of ionic spin states and the sample possesses ferromagnetic in nature and their application is in recording media where low coercivity is required when maintaining high saturation magnetization. Photo-Fenton activity for CoFe$_2$O$_4$ nanoparticles was examined by the degradation of MB with the synthesized catalyst under visible light irradiation. In this experiment 50 ml of 10 mg/l of MB aqueous solution was taken in which 50 mg of photo-catalyst was dispersed. Before irradiating, the suspension was kept in the absence of light for 30 minutes to ensure desorption-adsorption equilibrium and then the solution with the catalyst was out in the open visible light before irradiation H$_2$O$_2$ was added. At given time intervals, 3 ml of aliquots were taken and centrifuged. The intensity of MB was determined with the help of UV-vis spectrophotometer. Hence presence of light with the catalyst the degradation was found to be 99.8% within 100 minutes shown in Fig.7. Hence, it can be proved that CoFe$_2$O$_4$ nanoparticle has a potential photo-Fenton activity.

**Summary.** In précis, inverse spinel CoFe$_2$O$_4$ nanoparticles were successfully synthesized using co-precipitation technique, resulting into favorable magnetic, optical properties and small particle size. X-ray diffraction revealed the formation of cubic spinel structure CoFe$_2$O$_4$ nanoparticles. In FTIR spectrum, the foremost band at 549 cm$^{-1}$ corresponds to metal-oxygen, stretching vibrations located at octahedral and tetrahedral positions. The TEM image of CoFe$_2$O$_4$ nanoparticles gives an idea about the distribution of spinel shape nanoparticles. VSM measurements revealed the weak ferromagnetic behavior from which the magnetic parameters were observed. Application of photo-fenton activity proved that the synthesized nanoparticle is an efficient catalyst in degradation of MB.

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