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XRD, IR and bandgap spectra of $CoFe_2O_4$ magnetic nanoparticles synthesized via sol-gel auto-combustion method; proposed for the photocatalytic applications

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Abstract.

The structural properties of $CoFe_2O_4$ ferrite nanoparticles have been studied after the fabrication of $CoFe_2O_4$ magnetic nanoparticles via sol-gel auto-combustion method assisted by $C_6H_8O_7.H_2O$ keeping a metal nitrate to citrate ratio at 1:3. The X-ray diffraction studies of $CoFe_2O_4$ magnetic nanoparticles were carried out to investigate the phase purity and the presence of impurities, if any. In this investigation, the XRD pattern revealed the presence of Bragg's reflections belongs to the inverse spinel; cubic structure; ferrite formation without any addition peak. The crystallite size (t) was estimated using Debye-Scherer's formula and reported according to the reported literature. We report the $CoFe_2O_4$ magnetic nanoparticles with a band gap yield 1.57 eV; lower than the reported available literature. We propose that the lower band gap of $CoFe_2O_4$magnetic nanoparticles should be studied further as it can be useful for the photo-catalytic applications, particularly in the degradation of methylene blue dye.

1. Introduction

In the recent days, the photo-catalytic research has been speeded up by the researchers all over the world, as the industry demand for energy and resources have a great concern about an environmental pollutant [1, 2]. Photo-catalytic H_2 production is of massive interest for the researcher, as it could be future fuel scope for the new generation without any geographic discrimination [3]. An effort was carried out to develop efficient photo-catalysts for feasible solar fuel conversion as the large-scale research on solar energy conversion technologies and thermochemical hydrogen production was understudy. In our investigation, we found that the low-band gap catalysts such as magnetic nanoparticles can be attractive for the photo-catalytic activity. The low-band-gap can absorb the maximum percentage of visible light in the particular wavelength range [4, 5].

Magnetic nanoparticles are being widely accepted in various fields viz. medical appliances [6], medical implants [7], medical diagnosis technologies [8], drug delivery systems, [9, 10], pharmaceutical ingredients [11], agriculture technologies like seed coating [12], anti-bacterial [13, 14] and anti-fungal seed [15] and crop protector, agricultural storage techniques [16], advanced functional materials, [17], environment pollution controlling devices, etc. Spinel ferrites are belong to the space group Fd-3m O_h^7[18] with a general chemical formula AB_2O_4 [19, 20]; where A is divalent transition metal ion like Cu^{2+}, Zn^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, etc. and B is trivalent ferrous (Fe^{3+}) respectively [21]. Various synthesis techniques have been investigated with by the researchers. Some of these synthesis methods are the ceramic method [22], sol-gel auto-combustion [23], ultra-fast pyro-synthesis [24], electro-deposition method [25], chemical co-precipitation method [26], micro-emulsion [27], etc. Here, we propose the synthesis of $CoFe_2O_4$ magnetic nanoparticles via the sol-gel auto-combustion.

2. Synthesis of $CoFe_2O_4$ magnetic nanoparticles

AR grade quality chemicals were used for the synthesis and Cobalt nitrate hexahydrate [$Co(NO_3)_2.6H_2O$], ferric nitrate nonahydrate [$Fe(NO_3)_2.9H_2O$], and citric acid ($C_6H_8O_7.H_2O$) as fuel were used as an initial starting material for the synthesis process of spinel structured $CoFe_2O_4$

magnetic nanoparticles. NH_3 was considered for maintaining the pH at 7 assumed to be neutral level for the photo-catalytic activity examination. In the sol-gel processing technique of $CoFe_2O_4$ magnetic nanoparticles can be described in various ways; out of which halogenations of 'sol'; 'gel' formation; 'dry-gel' (80-90°C); ignition at proper temperature and Auto-combustion (<200 °C) at high temperature. The sol-gel is renown to be low-temperature method, but in sol-gel auto-combustion; the after ignition temperature may goes to higher range (depending upon the reaction conditions). In the synthesis of $CoFe_2O_4$ magnetic nanoparticles, metal nitrates were mixed with the citric acid ($C_6H_8O_7.H_2O$) with the ratio of 1:3. The magnetic model of the $CoFe_2O_4$ can be represented as Eq. 1 and Eq. 2;

$$(Co_x Fe_{1-x})[Co_{1-x} Fe_{1+x}]O_4 \qquad (1)$$

$$\uparrow 3_{(x)}\ \mu B \uparrow 5_{(1-x)} \downarrow 3_{(1-x)}\ |\ \mu B \downarrow 5_{(1+x)}\ \mu B \qquad (2)$$

The continuous heat treatment and stirring lead to form a 'gel'. The resulting 'gel' has to be continued for the chemical redox reactions with an increase in temperature up to 120-140 °C, which forms a 'dried gel' in a beaker. At a particular condition the 'dry-gel' gets ignited to bring out the auto-combustion process. The fluffy loose powder can be termed as a premature nanopowder, which was grounded using a mortar pestle. Post-sintering at 850 °C for 24 h, we got the final product of $CoFe_2O_4$ magnetic nanoparticles.

3. Results and discussions:

3.1. Structural analysis of CoFe2O4 magnetic nanoparticles

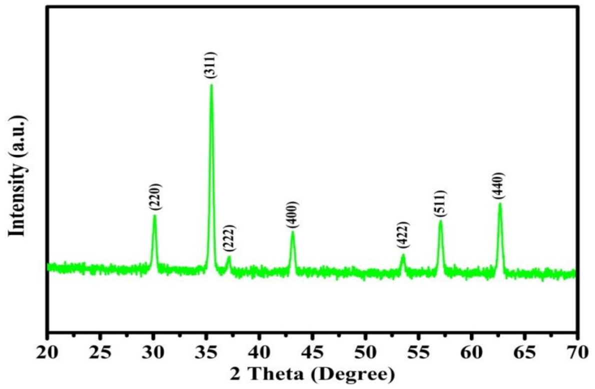

Fig 1. XRD pattern of $CoFe_2O_4$ magnetic nanoparticles

X-ray diffraction pattern of sol-gel synthesized $CoFe_2O_4$ magnetic nanoparticles was taken at room temperature by Philips X-ray diffractometer Model RIGAKU Miniflex 600 using Cu-Kα radiation (λ = 1.5406 Å). In the present study, phase purity investigation and structure analysis of the $CoFe_2O_4$ magnetic nanoparticles was carried out by the XRD technique. X-ray diffraction was recorded in the 2θ range for 20° to 70°. All the major reflections were indexed using Bragg's law.

Here, the Fig. 1 shows the XRD pattern of $CoFe_2O_4$ magnetic nanoparticles, in which intense Bragg's reflections (220), (311), (222), (400), (422), (511) and (440) suggested the FCC type inverse spinel; cubic structure, ferrite phase formation [28, 29]. All the reflections were indexed using the Full Proof program. No extra peak was observed in the XRD pattern. Bragg's condition for diffraction maxima is given by Eq. 3;

$$n\lambda = 2d_{hkl}\sin\theta \qquad (3)$$

Where, d is the interplanar spacing of two planes, (a) is the lattice constant, and (hkl) is the Miller indices of each plane. In the present structural situation, an ionic radius of Co^{2+} (0.78 Å); Fe^{2+} (0.74 Å); Fe^{3+} (0.64 Å) [30, 31] in the $CoFe_2O_4$ magnetic nanoparticles has the combined cause-effect which reflects in the lattice constant (a) [32].

3.2. Infra-red spectroscopy of $CoFe_2O_4$ magnetic nanoparticles

The functional group analysis of $CoFe_2O_4$ magnetic nanoparticles was carried out by IR spectroscopy. Infrared spectroscopy was recorded by Perkin-Elmer spectrophotometer using KBr pallet at room temperature in the wavenumber range of 4000-350 cm^{-1}. IR spectroscopy is a common characterization used to confirm the functional group present in the $CoFe_2O_4$ magnetic nanoparticles and the stretching vibrations (M-O) bands associated with the structure; particularly for ferrites. In Fig. 2, we report the frequency band υ_1 = 418 cm^{-1} correspond to the intrinsic vibration of the tetrahedral group complexes Fe^{3+}- O^{2-} and υ_2= 541 cm^{-1} which corresponds to the octahedral group complexes Fe^{3+}-O^{2-}.

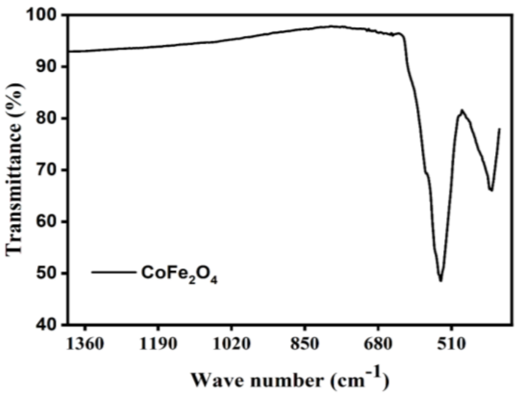

Fig 2. FTIR of $CoFe_2O_4$ magnetic nanoparticles

3.3. Bandgap of CoFe2O4 magnetic nanoparticles

The UV-Vis spectroscopy was performed for the $CoFe_2O_4$ magnetic nanoparticles. The optical properties of the investigated sample report the band gap in the range 1.57 (±1) eV which is lower in comparison to the available reports which were studied for the present investigation.

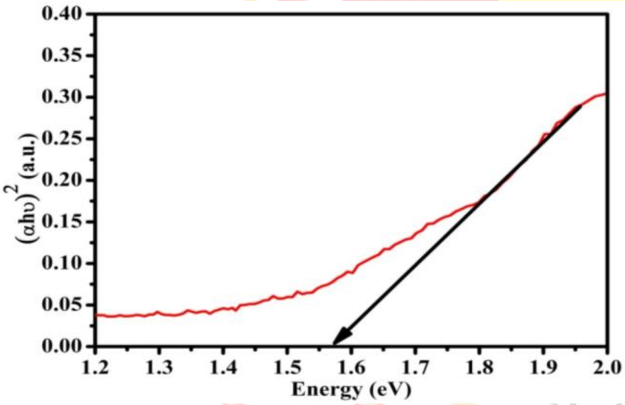

Fig 3. Band gap (E_g) of pure $CoFe_2O_4$ magnetic nanoparticles

Fig. 3 depicts the energy diagram (Energy vs. $(\alpha h\nu)^2$) indicating band gap spectra of $CoFe_2O_4$ magnetic nanoparticles. The low value of band gap may be found useful for the methylene blue dye degradation in particular. The sol-gel synthesized $CoFe_2O_4$ magnetic nanoparticles could be employed to study the hole scavenger property and chemical stability over the high pH value during the photo-catalysis.

4. Conclusions

In this investigation, we have successfully fabricated $CoFe_2O_4$ magnetic nanoparticles via the sol-gel auto-combustion method using $C_6H_8O_7$. H_2O as a fuel. The $CoFe_2O_4$ magnetic nanoparticles were characterized by XRD, IR and optical spectra. The XRD pattern suggested that $CoFe_2O_4$ magnetic nanoparticles belong to the inverse spinel; cubic structure ferrite phase, with no extra peak. From the Infra-Red spectra, we report the frequency band υ_1 = 418 cm^{-1} and υ_2 = 541 cm^{-1} which suggests the formation of ferrite phase. The optical bandgap was reported to be 1.57 eV which was found to be lower in comparison to the reported literatures. The lower bandgap of $CoFe_2O_4$ magnetic nanoparticles may be useful for the photo-catalytic degradation of methylene blue dye in particular.

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Conflicts of interest

The authors have no conflict of interest.

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