PHOTOCATALYTIC STUDY USING La-Ag AND Ni-Ag DOPED COBALT OXIDE NANOPARTICLES AS PHOTOCATALYST

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ABSTRACT

The present work deals with the synthesis of La-Ag and Ni-Ag doped cobalt oxide nanoparticles, their characterization by FT-IR, XRD, SEM, TEM analyses and photo dye degradation study using the doped cobalt oxide NPs as catalyst. The study shows the efficacy of doped cobalt oxide NPs to degrade the dyes viz. Methyl Orange (MO) and Methylene Blue (MB) by irradiation with light. Considering unique band energy gaps associated with the nanostructured cobalt oxide NPs, the study deals with photo dye degradation efficiency of doped Co_3O_4 NPs analyzed with UV-Vis spectroscopy. Following the synthesis of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 NPs using thermal decomposition method, photo dye degradation study was carried out with varied time intervals.

KEYWORDS: UV-Vis spectra, Photo dye degradation, Methyl Orange (MO), Methylene Blue (MB).

INTRODUCTION

In recent decades, globally facing problems with pollutants and contaminants by using different types of dyes as it discharges high content of organic and inorganic substances. About 800,000 tons per year production of worldwide in manufacturing industry, textile industry, etc. Untreated discharge of effluents from several manufacturing industries commonly contains synthetic dyes that harm the aquatic living [1,2]. Synthetic dyes which are used in industries show considerable diversity such as azo, anthrax quinone, sulphur, indigoid, triphenyl methyl (trityl), and phthalo cyanine derivatives [3]. The toxicity of dye that has chemical content can initiate substantial environmental pollution and serious health-risk factors [4]. Cobalt oxide nanoparticles have adequate band hole for the corruption of colours [5-8].

Photo degradation, a process in which a substance breaks down or undergoes structural changes under the influence of light, is a significant area of study with wide-ranging applications. In recent years, the integration of nanoparticles into this field has opened up new avenues for enhancing the efficiency and selectivity of photo degradation processes.

Nanoparticles, due to their unique size-dependent properties, have demonstrated remarkable potential in catalysing and accelerating photo degradation reactions [9].

The utilization of nanoparticles in photo degradation processes has gained considerable attention across various scientific disciplines, including environmental science, materials science, and nanotechnology. These nanoparticles, often tailored for specific applications, play a crucial role in promoting photo catalytic reactions, where light energy is harnessed to initiate chemical transformations. This introduction marks the convergence of two dynamic fields - nanotechnology and environmental science, highlighting the promising role of nanoparticles in advancing the understanding and application of photo degradation processes. As we move deeper into this synergy, we explore the mechanisms, challenges, and potential solutions associated with leveraging nanoparticles for enhanced photo degradation efficiency. Cobalt oxide nanoparticles have been investigated for their catalytic properties in various chemical reactions, including photocatalytic dye degradation. Hence, an attempt has been made to explore the photocatalytic dye degradation capability of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles towards an azo dye (Methyl orange) and a thiazine dye (Methylene Blue).

EXPERIMENTATION

Materials and Methods

$Co(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $AgNO_3.6H_2O$, $La(NO_3)_2.6H_2O$, Phenyl acetic acid ($C_6H_5CH_2COOH$), Hydrazine hydrate (99% and density-1.032 g/ml), Diethyl ether $(CH_3CH_2)_2O$, Carbon tetrachloride (CCl_4), Conc. HCl, Potassium Iodate (KIO_3) were purchased from Hi-media and used for the research work. All the chemicals used were of analytical grade and used without any further purification. Double deionised water was used throughout the work.

Chemical Synthesis of La-Ag doped and Ni-Ag doped Cobalt Oxide Nanoparticles

Precursors were prepared using Co-precipitation method with cobalt nitrate with appropriate proportions of metal salts, phenyl acetic acid and hydrazine hydrate to obtain $[(La_{0.2}Ag_{0.2}Co_{0.6}(C_6H_5CH_2COO)_2(N_2H_4)_2]$ and $[(Ni_{0.2}Ag_{0.2}Co_{0.6}(C_6H_5CH_2COO)_2(N_2H_4)_2]$. The obtained precursors were calcined using at about 500^0C. The acquired black powdery substances were characterized by FT-IR, XRD, SEM, TEM and UV-Vis spectroscopy techniques.

Physico-Chemical Techniques

FT-IR spectra of the calcined doped metal oxide samples were been recorded using SHIMADZU with pressed KBr pellets. X-ray patterns were recorded for the metal oxide NPs samples using X'pert Pro P analytical instrument. The calcined samples' morphological studies were done using FE-SEM analyzer (Zeiss-Gemini 300 SEM). Using SHIMADZU/206- 26300-48, UV-vis spectrophotometry along with photodyedegradation studies were carried out.

RESULTS AND DISCUSSION

FT-IR spectroscopy

FT-IR spectra of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles are shown in **Figure 1**, which aids in understanding how doping affects the nanoparticle properties, like catalytic activity, electronic structure etc., In the FT-IR spectra of both the samples, two strong peaks appearing at 658 cm^{-1} and 558 cm^{-1} affirm the formation of a Co_3O_4 spinel oxide associated with Co^{3+} in Octahedral site and Co^{2+} in tetrahedral site [10].

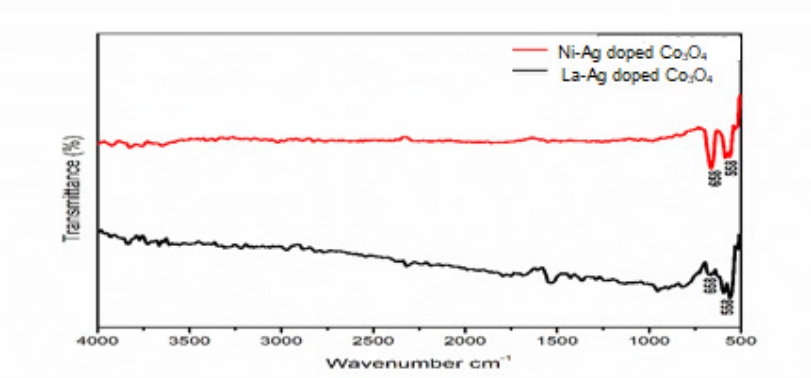

Fig.1 - FT-IR spectra of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles

XRD ANALYSIS

The XRD pattern of Co_3O_4 shows (hkl) values at (111), (220), (311), (400), (511) and (440) at 2θ angles of 23.34˚, 33.64˚, 41.00˚, 59.1˚ and 65.9˚ respectively, which can be readily indexed to face centered cubic with Fd3m (JCPDS card No.80-1535) [11]. It can be observed from the XRD pattern that the doped Nickel, Silver and Lanthanum, Silver ions have been partially incorporated into the cobalt lattice sites without major distorting crystal symmetry.

The crystallite sizes of both the samples calculated from the Full Width at Half Maximum (FWHM) from their respective strongest peaks at (311) and (220) using Scherrer's equation,

$$D = K \lambda / \beta \cos \theta$$

where λ is the wavelength of X-ray, D is the average crystallite size, β is the FWHM, θ represents the Bragg's angle at the corresponding peak and K is the instrumental constant, were found to fall in the range 11-14 nm.

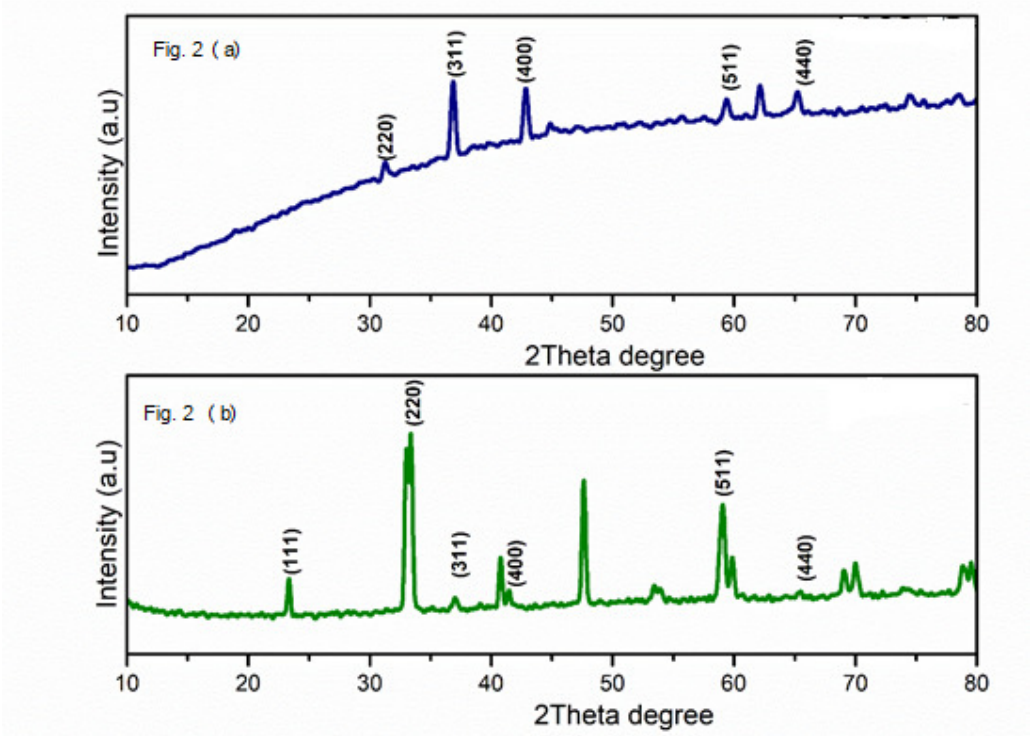

Fig. 2 (a) - XRD Pattern of La-Ag doped Co_3O_4 nanoparticles

Fig. 2 (b) - XRD Pattern of Ni-Ag doped Co_3O_4 nanoparticles

SEM and EDAX Analyses

Figures 3a and 3b respectively show the morphology of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles. Both the nanostructured samples are seemed to possess enhanced physico-chemical properties such as surface phenomena and catalytic stability. The nanoparticles appear to have angular, plate-like structures with sharp edges and corners. The particles remain clustered, forming larger agglomerates. This suggests a strong tendency for these particles to stick together, possibly due to van der Waals forces or other intermolecular interactions.

The EDAX spectra of both samples clearly demonstrate the presence of elements like Ni, Ag, Co and O, and La Ag, Co and O respectively. These results are consistent with the XRD patterns, implying the purity of the sample.

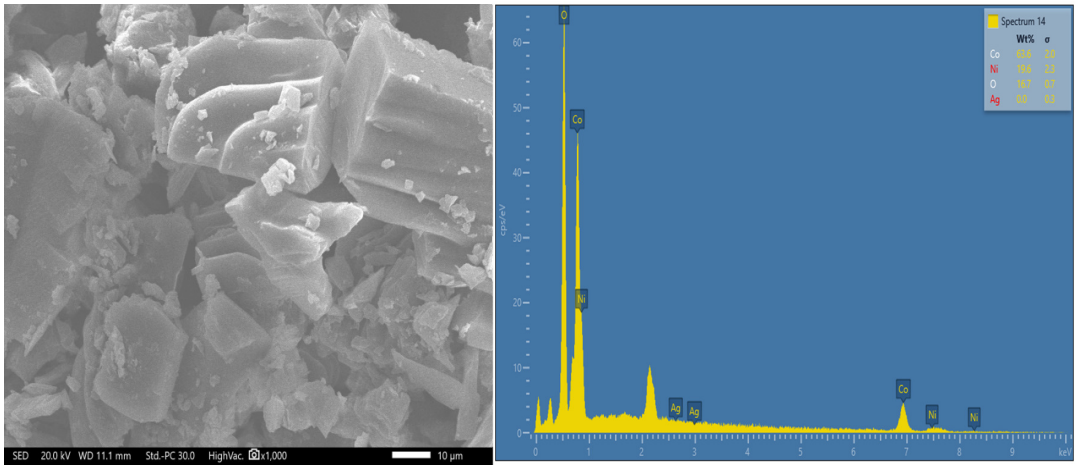

Fig (3a)

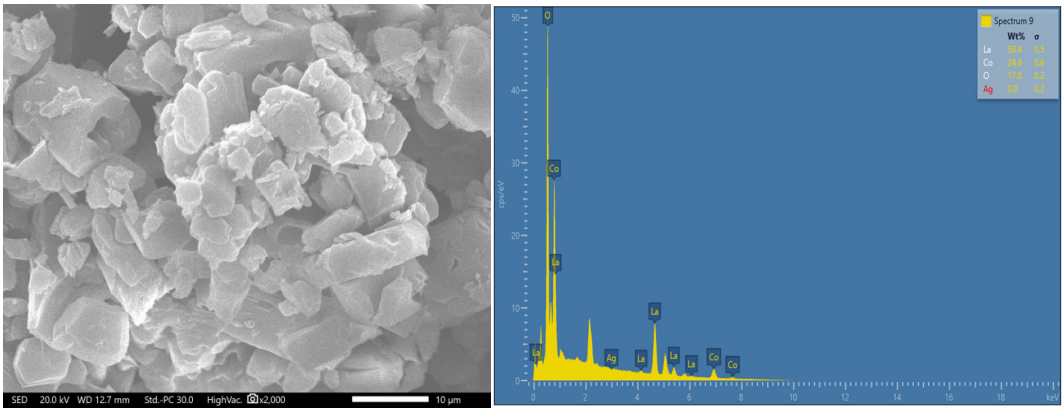

Fig (3b)

Fig. (3a &3b) - SEM images and EDAX spectra of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles

HRTEM Analysis

Figures 4 (a & b) show the HRTEM images and SAED patterns of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles respectively. The presence of some bigger particles can be attributed to be the aggregation or overlapping of some small particles, due to their magnetic induction. The average grain size observed from the micrograph is about 11-13 nm, which is in agreement with the calculation using Scherrer's equation. Fig. 3.5 shows that the SAED pattern consists of sharp rings, which reveal the polycrystalline nature of the nanoparticles.

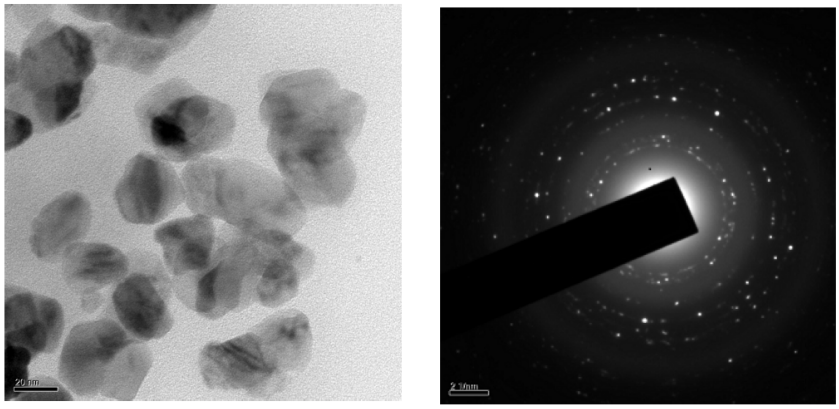

Fig (4a)

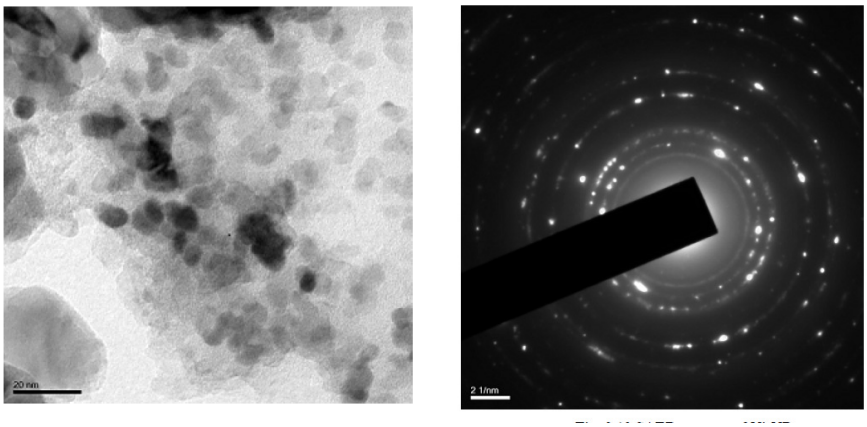

Fig (4b)

Fig. (4a &4b) - HRTEM images and SAED patterns of La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles

PHOTO CATALYTICAL STUDY

The photo catalytic activity of the synthesized NPs has been investigated using Methyl Orange and Methylene Blue dye. A tremendous physical and chemical techniques like chlorination, ultra filtration, ozonation and coagulation helps degradation of dyes and secondary pollution issues are confronted [12].

The above said application was mostly prepared as bulk material using co-precipitation method [13-15]. The experiment was performed using freshly prepared MO and MB aqueous solution taking 5 mg/500 ml. Before the initiation of light irradiation, about 50 mg of synthesized catalyst was added to 100 ml freshly prepared dye solution. The catalyst solution is stirred for 45 min under dark using magnetic stirrer in order to attain the adsorption-desorption equilibrium. Subsequently, the solution was irradiated using 20W compact lamp

with 130 cd. The sample solution is collected with varied time interval of 0-75 min for every 15 min. The dye solutions MO and MB have the nature pH of 4.2 and 6.5 respectively. The absorbance values of MO were found to be at 460 nm and 463 nm for MO-La-Ag doped Co_3O_4 and MO-Ni-Ag doped Co_3O_4 respectively, while that of MB were found at 255 nm and 257 nm respectively for MB-La-Ag doped Co_3O_4 and MB-Ni-Ag doped Co_3O_4 respectively using UV-Vis spectrophotometer as shown in figures 4a, 4b, 4c and 4d.

To determine the photo catalytic efficiency of MO and MB, the following equation has been applied;

$$\textbf{Photo dye degradation \%} = \frac{C_0 - C}{C_0} \times 100$$

where C_0 is the initial concentration of the dye and C is the concentration of the dye at time t. As it has been referred that photo catalytic property increases with the number of dopants is increased. In heterogeneous photocatalytic degradation, the efficiency is higher as the number of reactive oxygen sites is greater and the OH radicals than in single species.

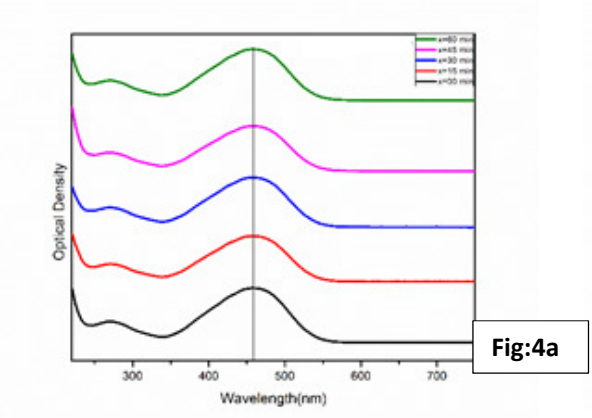

Fig:4a

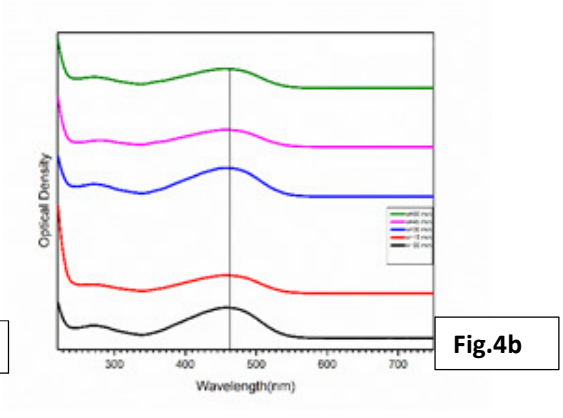

Fig.4b

Fig. 4a - UV-vis absorbtion plot for MO-La-Ag doped Co_3O_4 nanoparticles

Fig. 4b - UV-vis absorbtion plot for MO-Ni-Ag doped Co_3O_4 nanoparticles

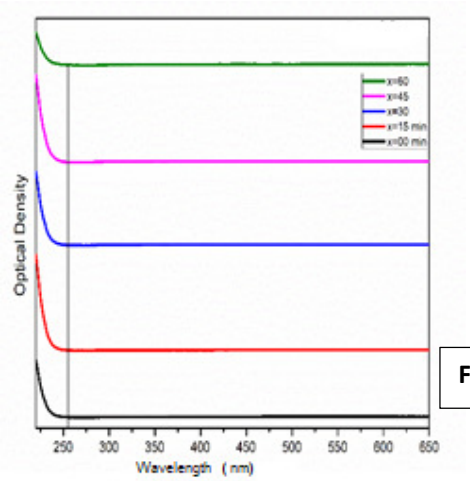

Fig:4c

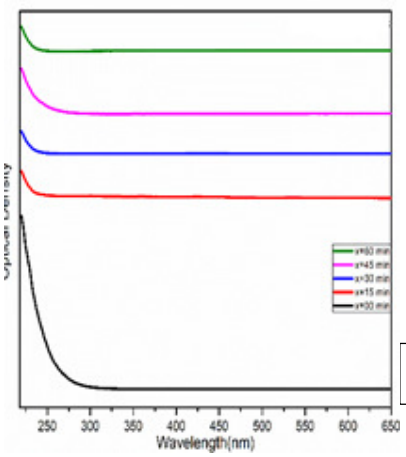

Fig: 4d

Fig. 4c - UV-vis absorbtion plot for MB-La-Ag doped Co_3O_4 nanoparticles

Fig. 4d - UV-vis absorbtion plot for MB-Ni-Ag doped Co_3O_4 nanoparticles

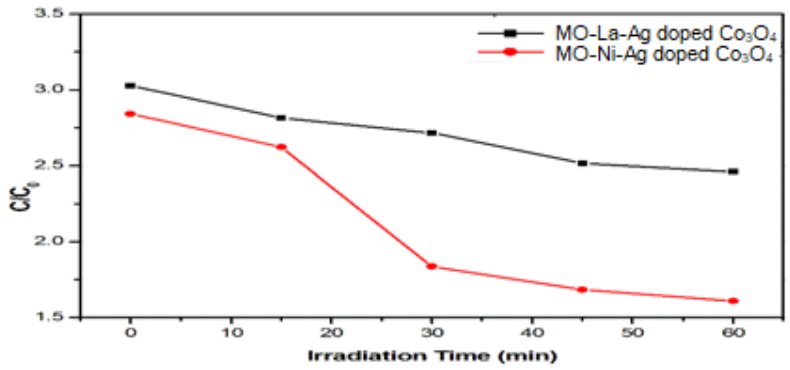

Fig. 5 Photo dye degradation of MO-La-Ag doped Co_3O_4 and MO-Ni-Ag doped Co_3O_4 nanoparticles

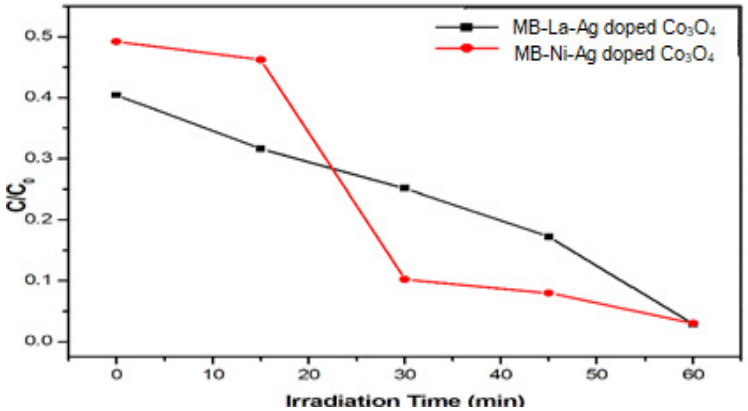

Fig: 6

Fig. 6 Photo dye degradation of MB-La-Ag doped Co_3O_4 MB-Ni-Ag doped Co_3O_4 nanoparticles

In MO-La-Ag doped Co_3O_4, the concentration ratio decreases gradually over time, starting at around 3.0 and reaching slightly above 2.5 at 60 minutes, whereas in MO-Ni-Ag doped Co_3O_4, the concentration ratio decreases more rapidly, starting at around 3.0 and reaching approximately 1.5 at 60 minutes. The former shows a faster and more significant reduction in concentration compared to the latter under the same irradiation conditions. This suggests that MO-La-Ag doped Co_3O_4 are more effective in reducing the concentration over the given time period.

In MB-La-Ag doped Co_3O_4, the concentration ratio drops steadily over time, reaching approximately zero around 60 minutes, while in MB-Ni-Ag doped Co_3O_4, the concentration ratio decreases more quickly, reaching approximately zero around 50 minutes (Fig. 6). The MB-La-Ag doped Co_3O_4 nanoparticles show a rapid reduction in concentration compared to MB-La-Ag doped Co_3O_4 the under similar conditions. This implies that MB-Ni-Ag doped Co_3O_4 nanoparticles are found to be more effectual in reducing the concentration over the given time period than that of MB-La-Ag doped Co_3O_4 nanoparticles.

Moreover, the corresponding band gap energies of MO-La-Ag doped Co_3O_4 and MO-Ni-Ag doped Co_3O_4 nanoparticles and, MB-La-Ag doped Co_3O_4 and MB-Ni-Ag doped Co_3O_4 nanoparticles were calculated as 5.3eV, 5.2eV and 5.3eV, 5.1eV respectively using Tauc's formula as shown in Fig.7.

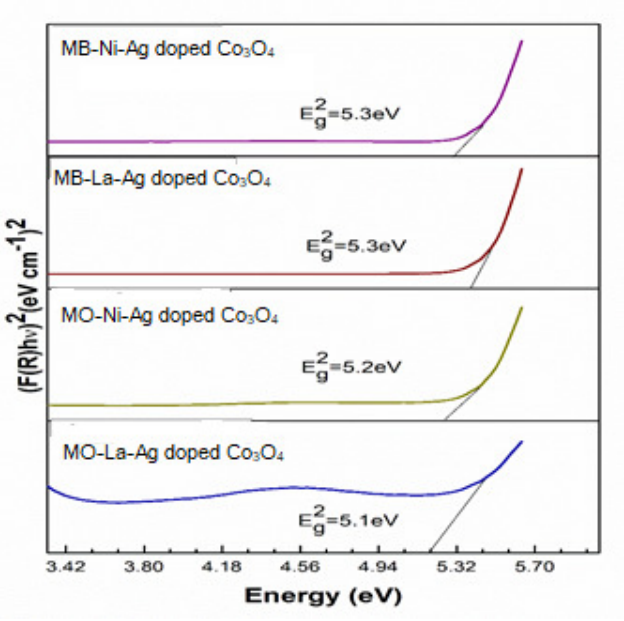

Fig. 7-Tauc Plot of Methyl Orange and Methylene Blue dye with La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles

CONCLUSIONS

In brief, La-Ag doped Co_3O_4 and Ni-Ag doped Co_3O_4 nanoparticles were synthesized using thermal decomposition method. XRD studies affirmed the presence of nanoparticles of size varying from 11-14 nm in both samples, which was in agreement with the HRTEM results as well. SEM images of both the samples showed plate-like structures. The UV absorption depicted the shifts in the bandgap due to the non-uniform size of the nanoparticles. The photo catalytic activities of the samples towards Methyl Orange and Methylene Blue dye showed noticeable degradation in short period of time.

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