Piper Nigrum Mediated Green Synthesis, Charecterization of Undoped Cobalt Oxide and Cerium Ion Doped Cobalt Oxide Nanoparticles

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Abstract: - An eco-friendly green synthesis of cobalt oxide nanoparticles using seed extract of piper nigrum was investigated. Synthesized nano Cobalt oxide were characterized using UV-Vis, FT-IR spectroscopic techniques and AFM. UV spectra showed the maximum absorbance of 268 and 305 nm due to the excitation of surface Plasmon vibrations in the cobalt oxide nanoparticles formation. FTIR spectrum exhibited the characteristic band at 704 cm-1 which indicated the O-Co-O bridging vibration of Co_3O_4nanoparticles. Photocatalytic degradation of Crystal violet under UV-irradiation was also investigated. Undoped and Ce ion doped cobalt oxide nanoparticles possess photocatalytic activity while the latter shows enhanced degradation efficiency percentage and can be used as an effective photocatalyst.

Keywords: Co_3O_4, Nanoparticles, Green synthesis, Piper nigrum, XRD,etc.,

INTRODUCTION

Cobalt oxide (Co_3O_4) nanoparticles have potential application in various areas including optical, magnetic, high catalytic efficiency and fast electron transfer kinetics for biosensing purposes [1-3]. Cobalt oxide in an inorganic compound.Co_3O_4 adopts the normal spinal structure with the Co^{2+} ions tetrahedral interstices and Co^{3+} ions in octahedral interties of the cubic close-packed lattice of oxide ions. Co3O4 belongs to the normal spinal structure, which is based on a cubic close packing array of oxide ions in which Co (II) ions occupy the tetrahedral 8a sites and Co(III) ions occupy the octahedral 16d sites. Synthesis of cobalt oxide nanoparticles have been obtained by different methods as solvothermal, mechanocemical, reduction–oxidation, sol-gel and polymer combustion, generating different morphologies like nanotubes,nanorods, nanocubes, and spherical particles[4]. Cobalt oxide nanoparticles have been synthesized by various methods like sol-gel, surfactant-mediated synthesis, thermal decomposition, poly-matrix assisted, several method have been developed to prepare ultrafine Co_3O_4 powder, including low pressure spray pyrolysis.

II. EXPERINMENTAL METHOD

To precursors Ammonium Ceric sulphate $[(NH_4)_4Ce(SO_4)_4]$, Cobalt chloride and Crystal violet were purchased from Himedia company. All solutions are made up with deionised water.

2.1. Collection of Seed materials

Fresh seeds of Piper Nigrum were procured from the market of Thoothukudi district, Tamilnadu. The fruits were washed well with water; shade dried, powdered, sieved and stored separately. The fine powder thus obtained was used for the seed extract preparation.

2.2. Preparation of 0.1M Ammonium Ceric Sulphate solution

0.1M Cobalt chloride solution was prepared by dissolving 2.37g of Cobalt chloride in 100mL of double distilled water in a standard measuring flask. The Cobalt chloride solution was prepared fresh each time and used immediately.

2.3. Preparation of Piper Nigrum seed extract:

To prepare the seed extract, 10 g piper Nigrum seeds are weighed and grind to a powdered form. The powdered sample is boiled with 100mL of distilled water in a 250mL beaker. The mixture was heated for 10 minutes. The resulting solutions were filtered through WhattmanNo.41 filter paper, collected, labeled and stored in refrigerator for further use in the synthesis of Co_3O_4 nanoparticles.

2.4 Synthesis of undoped cobalt oxide nanoparticles and Ce ion doped cobalt oxide nanoparticles using piper Nigrum seed extract:

Cobalt oxide nanoparticles were synthesized by green method.100ml of Piper Nigrum seed extract and 0.1N of cobalt chloride solution are mixed and with is stirred with the help of magnetic stirrer for about 30minutes. Then it is refluxed at an elevated temperature of for 2 hours. The brown coloured cobalt oxide nanoparticles so obtained are filtered through the whatmannNo.41 filter paper and was used for the further characterization studies and applications. Similar procedure was adopted for the synthesis of cobalt oxide nanoparticles using Ceric ammonium sulphate as the precursor.

2.5. PHOTOCATALYTIC ACTIVITY

Nano sized cobalt oxide is a good photo catalyst to degrade organic contaminants as a crystal violet. The photocatalytic degradation of crystal violet dye using Co_3O_4 nanoparticles is investigated with the following process:

About 0.1g of synthesized un-doped and doped cobalt oxide nanoparticles were mixed with 100ml of 10mg of crystal violet dye solution. The suspension was constantly stirred for 60 minutes in the dark before irradiation to reach equilibrium absorption and desorption of doped and un-doped cobalt oxide nanoparticles in the organic dye solution. Then the suspension was placed in a closed chamber and irradiated with sunlight. All six set of reaction were observed one by one in every time interval of 10 minutes for 1hr. Finally the rate of decomposition was monitored by taking 1ml of samples from each set and recording the UV- visible Spectra in the wavelengths. A Blank experiment was carried out without addition of nano catalysts. The degradation of crystal violet dye solution was monitored for 3 hrs. The rate of decomposition of the dye is calculated by recording the UV-Vis spectra after centrifugation and filtration.

2.7. INSTRUMENTATION

Computer controlled JASCO V-650 was used to study UV-Vis spectral behaviour.The FT-IR spectra were recorded using a Nicolet iS5 instrument. The surface morphology of the nanoparticles was studied using Carl Zeiss EVO 18 SEM operating at 15 KV using normal incidence. EDAX measurements were carried out by Quantax 200 with X-Flash-Bruker.

III. RESULT AND DISCUSSION

3.1. UV-VISIBLE SPECTROSCOPY

The UV-Vis spectra of undoped Co_3O_4 and Ce ion doped Co_3O_4 nanoparticles are shown in Fig.3.1& 3.2.The formation of Co_3O_4nanoparticles was confirmed by the absorption bands for undopedCo_3O_4nanoparticles at 296nm and 416nm [1,2]. It is effectively blue shifted when compared with the absorption wavelength (470nm) of bulk Co_3O_4 [3,4]. This blue shift is attributed to the smaller size of the synthesized nanoparticles and the quantum size effect [5, 6]. The absorption bands obtained from 250-450 nm indicates the charge transfer transition from $O^{2-}\rightarrow Co^{2+}$ and $O^{2-}\rightarrow Co^{3+}$ of Co_3O_4 [8] and Co (III) has octahedral site and the electronic transition is from $^1A_{1g}\rightarrow {}^1T_{2g}$. [7]

The absorption band for Ce ion doped Co_3O_4 nanoparticles was observed at 268 nm and 306 nm [8,9]. The absorption band obtained for Ce ion doped Co_3O_4 nanoparticles is found to have more absorption (hyperchromic) than the undoped Co_3O_4 nanoparticles. This might be due to the interaction between Ce ion and Co_3O_4 lattice [10]. The absorption bands are effectively blue shifted when compared to the wavelength of undoped Co_3O_4 nanoparticles appeared at 296nm and 410nm. The blue shift in this case is less when compared to the undoped Co_3O_4 nanoparticles, which in turn is considerably blue, shifted when compared to the bulk phase Co_3O_4.

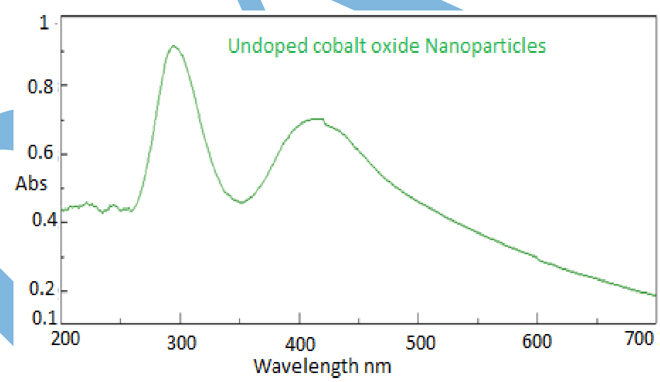

Fig 3.1 UV- Visible spectrum of Undoped Co_3O_4 nanoparticles synthesized using Piper Nigrum seed extract.

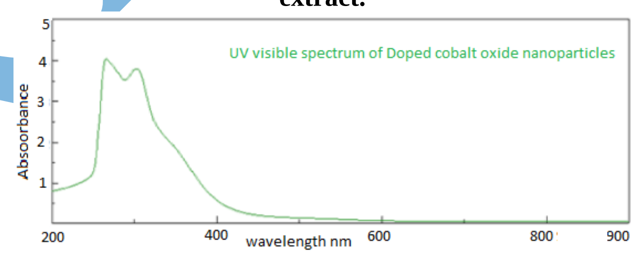

Fig 3.2 UV- Visible spectrum of Ce ion Doped Co_3O_4 nanoparticles synthesized using Piper Nigrum seed extract.

3.2. Fourier Transform Infrared spectroscopy

The FT-IR spectrum of undoped Co_3O_4 nanoparticles synthesized using aqueous seed extract of Piper Nigrum was shown in the Fig.3.3.The broad peak located at 3385 cm^{-1} can be assigned to the O-H stretching vibrations indicating the presence of hydroxyl group. The band appeared at 1653 cm^{-1} has been assigned Co-O vibration [14]. FT-IR spectrum of Co_3O_4nanoprticles showed significant absorption peak at 702cm^{-1}. The absorption band at 702cm^{-1} was assigned to the bridging vibration of O-Co-O bond. The absorption peak at 2919cm^{-1}may be due to the methyl stretching vibration.

The peak at 1315cm^{-1} was mainly attributed to C=N stretching frequency vibration as well as amide bond of proteins[11] .In addition there is a peak at 1436cm^{-1} corresponds to O-H bending of the hydroxyl group present [5]. The frequency observed at 901cm^{-1} corresponds to OH bending vibration of carboxylic group as present. The FT-IR spectrum of Ce-ion doped Co_3O_4nanoparticles synthesized using aqueous seed extract of piper Nigrum was shown in the Fig5.4. The broad peak located at 3370 cm^{-1} can be assigned to the O-H stretching vibrations indicating the presence of hydroxyl group. The band appeared at 1646 cm^{-1} has been assigned Co-O vibration.

FT-IR spectrum of Ce ion doped Co_3O_4nanoprticles showed significant absorption peak at 704cm^{-1}. The absorption band at 704 cm^{-1} was assigned to the bridging vibration of O-Co-O bond. The absorption peak at 2919cm^{-1}may be due to the methyl stretching vibration. The peak at 1318 cm^{-1} was mainly attributed to C=N stretching frequency vibration as well as amide bond of proteins. In addition there is a peak at 1436cm^{-1} corresponds to O-H bending of the hydroxyl group present. The frequency observed at 949 cm^{-1} corresponds to OH bending of carboxylic group as present [9]. The peak at 861 cm^{-1} is attributed to the stretching vibration of Ce-O bond. These stretching vibrations confirmed the interaction of Ce ions into the Co_3O_4 lattice.

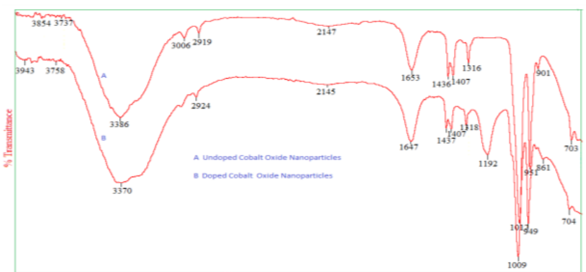

Fig. 3.3 FT-IR spectra of A) Undoped Co_3O_4 nanoparticles and B) Ce:Co_3O_4 nanoparticles Synthesized using Piper Nigrum seed extract.

3.3. Atomic force Microscopy (AFM)

3.3. AFM analysis of undoped and Ce ion doped Co_3O_4 nanoparticles synthesized using Piper Nigrum seed extract

Fig.3.4.shows the AFM spectral image of undoped Co_3O_4nanoparticles synthesized using Piper Nigrum seedextract with a scanning area of 2.461 pm^2 between 0 m X 1.56 µm and 0 m Y 1.56 µm. Spongy triangular nanoparticles [14] were found to be distributed over an irregular surface. The size is in the range of 30 nm -60 nm.

Fig.3.5. shows the AFM spectral image of Ce ion doped Co_3O_4nanoparticles synthesized using Piper Nigrum seedextract with a scanning area of 615.1 fm^2 between 0 m X 781 nm and 0 m Y 781 nm. The surface of Ce ion doped Co_3O_4 nanoparticles was found to be layered triangular like with irregular spherical nanoparticles with size in the range of 40 nm-60 nm.

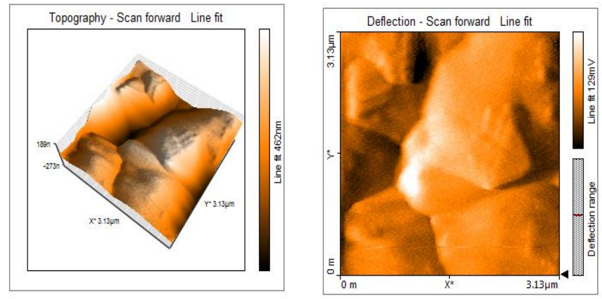

Fig.3.4. AFM spectral image of undoped Co_3O_4 nanoparticles synthesized using Piper Nigrum seed extract

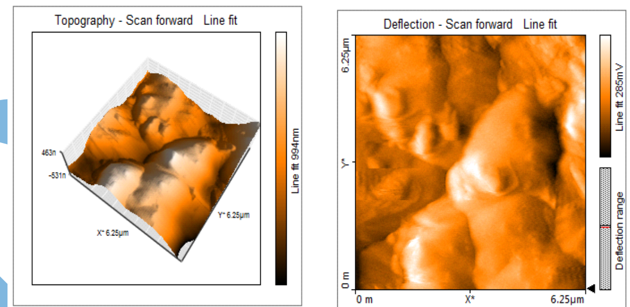

Fig.3.5.AFM spectral image of Ce ion doped Co_3O_4 nanopticles synthesized using Piper Nigrum seed extract

3.4. PHOTOCATALYTIC ACTIVITY:

The UV-Visible absorbance values of pure crystal violet dye solution shows absorption wavelength at 583 nm. The characteristic absorbance value at 583 nm was used tract the photocatalytic degradation process. The spectrum reveals that there was no formation of new product. The absorption peak at 220nm and 260nm can be attributed to the heterocyclic rings and benzene components respectively. The absorption peak decreased in intensity with increasing irradiation time, vanishing almost completely within 60 min. The rapid disappearance of the 583 nm absorption band suggests that the chromophore structure responsible for the characteristic dye is breaking down. In addition, opening of the benzene or heterocyclic rings underwent a speedy decolurization which is due to the bond breaking between aromatic rings.

The degradation efficiency of pure crystal violet dye with and without UV irradiation exposure was shown in Table .1 .It can be noticed from the recorded values that no significant changes of the concentration of crystal violet after 3hrs irradiation, which indicated that pure crystal violet dye solution cannot be easily degraded by UV light as shown fig.3.6 the degradation efficiency of pure crystal violet dye within the 3 hrs irradiation time was about 41 %.the result show that the photocatalytic activity of pure crystals violet dye was very less compared with the Ce ion doped cobalt oxide nanoparticles synthesizes using Piper Nigrum seed extract.

Fig.3.7 shows that the change in the absorbance spectra and the fluorescence quenching efficiency of crystal violet dye in the presence of Ce ion doped cobalt oxide nanoparticles synthesized using piper nigrum seed extract as photocatalyst. The crystal violet color was maximum disappeared after UV irradiation for 60mins as shown in Table.2. The decrease in absorption spectra of cobalt oxide nanoparticles at maximum wavelength of crystal violet dye is indicated by the degradation crystal violet dye in applied condition. After irradiation with UV light, the absorption intensity decreased due to the decolouration of the dye. The dye has almost disappeared after UV irradiation for 60 min and almost completed after 1 hr. The absorption intensity of crystal violet dye in the presence of doped cobalt oxide nanoparticles decrease with increasing irradiation time [12] when it is exposed in sunlight was shown in Table.2 respectively. The Degradation efficiency % has been calculated as

$$\boldsymbol{Efficiency} = \left[1 - \frac{C}{C0}\right] x100$$

Where Co is the initial concentration of the dye and C is the concentration of the dye at the selected irradiation time. The degradation efficiency of Ce ion doped cobalt oxide Nanoparticle towards crystal violet dye was shown in Table 1. The result shows that Ce ion deposited on the surface of cobalt oxide nanoparticle is more efficient for removal of crystal violet dye. The decolouration rate constant is determined by

$$\mathbf{ln(Co/C) = -Kt}$$

Co is the initial concentration of the dye and C is the concentration of the dye at the selected irradiation time and K is the rate constant. A plot of ln(Co/C) Vs Time represent a straight line and it was shown in Fig.3.9 The slope of which on linear regression equals the apparent first order rate constant. The rate constant was calculated to be 0.009 min^{-1}.of Ce ion doped cobalt oxide nanoparticles. A plot of ln(C0/C) Vs Time was shown in Fig 3.9. The slope of which on linear increasing is equal to the apparent of first order rate constant. The rate constant was calculated to be 0.009 min^{-1} of Ce ion doped cobalt oxide nanoparicles. From the above observation it was found that the metal loaded semiconductor possessed greater photocatalytic activity than pure semiconductor.

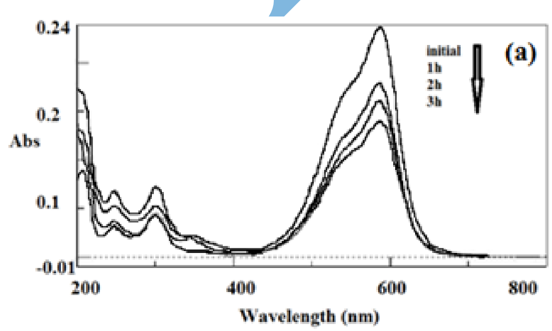

Fig.3.6.UV-Visible spectrum of pure Crystal dye

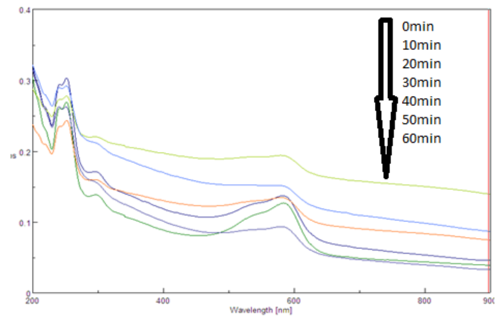

Fig.3.7.UV-Visible absorption spectra of crystal violet dye in the presence of Ce ion doped cobalt oxide nanoparticles using piper Nigrum seed extract

Table.1. Absorbance and degradation efficiency Values of pure crystal violet dye

Time (hr)	Absorbance	% Efficiency
Initial	1.4862	-
1	1.1985	24
2	1.1259	32
3	1.0540	41

Table.2. Absorption and degradation values of crystal violet dye in the presence of Ce ion doped cobalt oxide nanoparticles using piper Nigrum seed extract

Time (min)	Absorbance	% Efficiency
Initial	1.4862	-
10	0.3029	79.61
20	0.2920	80.35
30	0.2774	81.33
40	0.2689	81.69
50	0.2624	82.34
60	0.2433	83.62

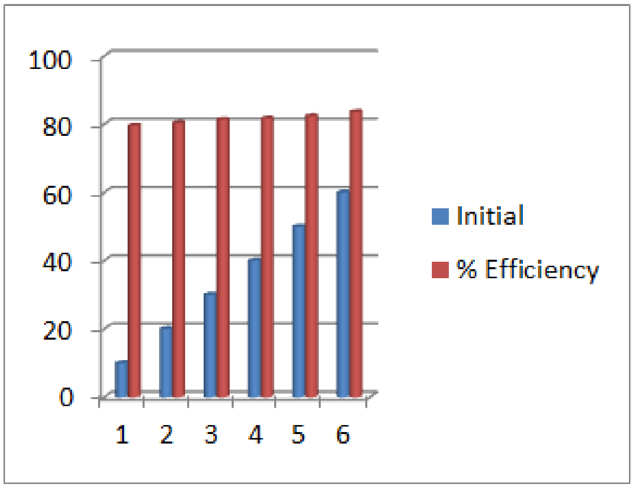

Fig.3.8.The % Efficiency of the Ce doped cobalt oxide nanoprticles

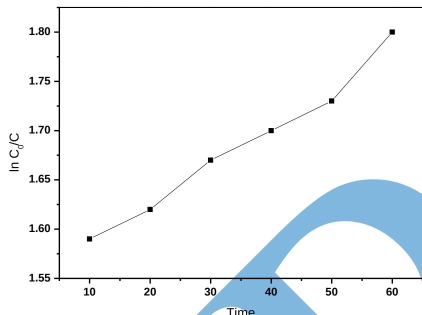

Fig.3.9.Degradation Plot of lnC0/C Vs Time

IV. CONCLUSION

In summary Cobalt oxide, cerium ion doped cobalt oxide nanoparticles were synthesized by green method using the aqueous seed extract of Piper Nigrum. The as- prepared un-doped and doped Co_3O_4 Nanoparticles were characterized using several techniques such as UV-Vis, FTIRand AFM. The size of the synthesized nanoparticle was in nm range AFM morphology showed a spongy triangular like morphology. The degradation efficiency of cerium doped Co_3O_4 Nanoparticles was higher. Hence it can be used as a catalyst for the removal of dyes from contaminated water resource. The Cerium doped Co_3O_4 Nanoparticles exhibit enhanced photocatalytic activity and can be efficiently used as photocatalyst in the process of removal of organic dyes and used for environmental cleaning and water purification.

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