

Synthesis and Characterization of Pure and Cu Doped CdO-TiO₂ Nanostructures for Photocatalytic Degradation of Rhodamine-B under Visible Light

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Abstract

In this work, attempts were made for synthesis and characterization of pure and Cu doped CdO-TiO₂ nanostructure materials which have been prepared by using cadmium acetate, tetra isopropyl orthotitanate, citric acid and copper acetate as starting materials. The formed samples were characterized by UV-Vis, FT-IR, SEM, and particle size analysis and find their photocatalytic activities. From UV spectrum, the optical properties of the prepared samples were determined. FT-IR spectrum reveals that the various functional groups present in the sample. SEM image shows the surface morphology of pure and doped CdO-TiO₂ nanoparticles. From particle analysis, the size of the particles present in the sample was determined. The prepared samples were used for the photodegradation of Rhodamine-B under visible light.

Keywords: CdO-TiO₂ nanostructure, FT-IR, SEM, photocatalytic activity and Rhodamine-B.

1. Introduction

In recent years, the industries such as paper, leather, rubber, plastics, textile, cosmetics, food and pharmaceutical industries are faced a lot of problems, due to organic pollutants released from various textile industries and chemical plants [1–5]. One of the biggest challenges we face within industry is refining toxic contaminants before discharging them into the environment [6, 7]. The techniques such as coagulation, flocculation, membrane filtration and adsorption [8-11] were used to eliminate colored contaminants (dyes) from waste waters. Among these methods, photocatalysis is one of the most effective and applicable method to eliminate the organic pollutants from waste water.

Researchers have studied several semiconductor metal oxides that are used to degrade a high number of recalcitrant materials in aqueous system [12]. The metal oxides such as TiO₂ and

CdO open a new era as a wide band gap semiconducting material. TiO_2 has a great extent of photocatalytic activity wide band gap,[13] high refractive index,[14,15] good chemical stability in adverse environment,[16] transparent to visible light,[14,15].

CdO is an n-type semiconductor has both direct and indirect band gaps of 2.5 eV and 1.98 eV, respectively [17]. CdO nanomaterials, due to its nature, are also potential candidate for photocatalytic activity. CdO nanostructures are low cost, chemically stable, and relatively nontoxic in nature [18,19] and are employed for a variety of applications in the field of photocatalysis [20], gas sensors [21], transistors [22], transparent electrodes [23] and solar cells [24,25]. In literature, successful preparation of titanium dioxide (TiO_2) coupled with cadmium oxide (CdO) by electro spinning method and its application in photocatalytic degradation under UV-light has been reported [26]. There are very few reports on the coupling of zinc oxide with cadmium oxide [27,28]

The present work discusses the synthesis of pure and doped CdO/ TiO_2 nanostructures by chemical co-precipitation method. The prepared samples are characterized by different techniques and are used for the photodegradation of Rhodamine-B under visible light.

2. Materials and Methods

2.1 Materials

Following analytical grade chemicals have been used for the synthesis of CdO/ TiO_2 nanostructure without any further purification. $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, tetra isopropyl orthotitanate, citric acid, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, NH_4OH deionized water (D.I.W), ethanol and Rhodamine-B (Rh-B) as raw materials.

2.2 Preparation of pure and Cu doped CdO- TiO_2 nanostructures

Pure and Cu doped CdO- TiO_2 material was synthesized by co-precipitation method. Initially, $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (1 M) was dissolved in anhydrous ethanol solution in beaker A and stirred well. Then 1 M of citric acid and tetra isopropyl orthotitanate in ethanol was taken as another solution in beaker B. The solution B was added to beaker A and stirred well. Then 2 drops of NH_4OH added to mixture and stirred well until the precipitate was formed. The obtained precipitate was washed with water and ethanol. Then obtained precipitate was collected and dried in the hot air oven for 12 h. Then the material is calcinated at 400°C for 4 hours.

For Cu doped CdO-TiO₂ material, 1 mmol of Cu(OAc₂)·H₂O was added initially to the Cd(OAc₂)·2H₂O containing beaker A while keeping the other conditions constant.

2.3 Characterization

Functional groups present in the prepared samples were confirmed by FT-IR spectrum. Optical absorptions of pure and Cu doped CdO-TiO₂ nanostructures was recorded using a Perkins–Elmer Lambda 35 UV–Vis spectrophotometer in the range of 100-1200 nm. The surface morphology of nanostructures was investigated by Scanning Electron Transmission Microscopy (SEM).

3. Results and Discussion

3.1 UV-Vis Analysis

The optical properties of the undoped and doped CdO-TiO₂ nanostructures were characterized by UV-Vis absorption spectroscopies and their corresponding spectra are shown in Fig. 1(a, b).

From Figure 1a, onset absorption peak of CdO-TiO₂ is shown about 410 nm and energy band gap value was calculated to be 2.60 eV. For Cu doped CdO-TiO₂ the absorption peak is about 311 nm. From absorption spectra, the energy band gap value was calculated to be 2.99 eV [18] . It was approximately equal to the theoretical value.

In theoretical method the band gap was calculated by using the formula

$$E=hc/\lambda$$

Where, h is Plank’s constant; C is velocity of light; λ is cut-off wavelength.

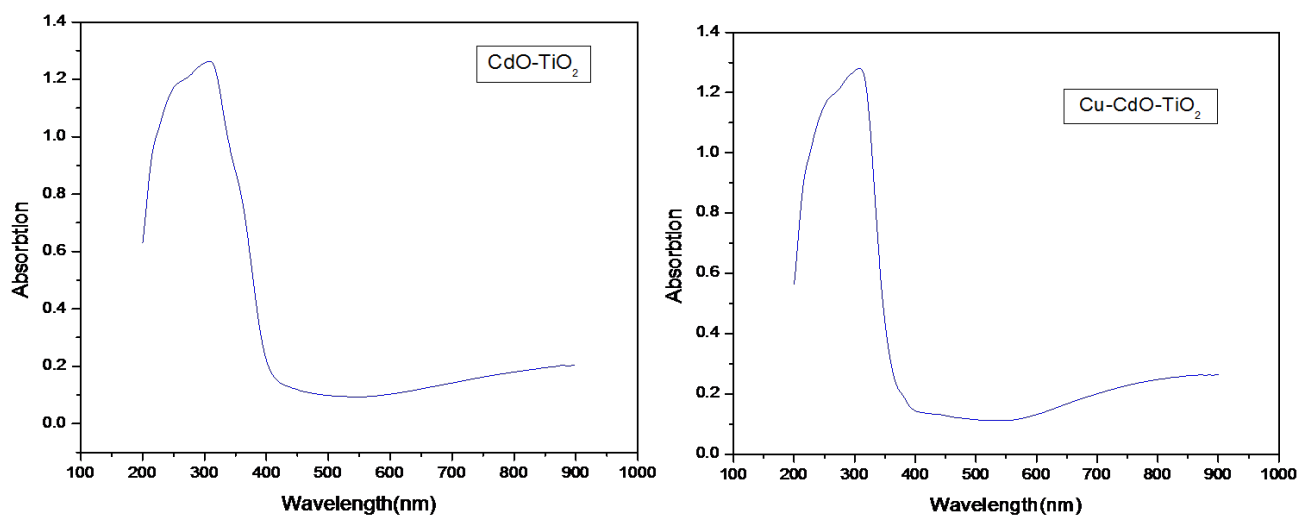


Figure 1 UV-Vis spectrum of (a) pure and (b) Cu doped CdO-TiO₂ nanostructure

3.2 FT-IR Analysis

FT-IR spectral analysis of the pure and Cu doped CuO/TiO₂ nanostructures were recorded and their spectra are shown in fig.2 and 3. FT-IR studies on the prepared nanoparticles were carried out over the range of 400-4000 cm⁻¹

From the fig 2, the absorption frequency bands are assigned at 3807.56, 3787.45, 3411.54, 2925.36, 2361.31, 2340.24, 1562.74, 1384.63, 1068.21, 1020.40, 783.65, 691.28, 554.71 and 466.96 cm⁻¹. The peaks at 3411.54 and 2925.36 cm⁻¹ represent OH group and C-H bond of the sample. The peaks at 1384.63 and 1068.21 cm⁻¹ corresponds to Ti-O bond C-O-C group. The absorption bands at 783.65 cm⁻¹ corresponds to Cd-O bond and at 554.71 cm⁻¹ corresponds to Ti-O-Ti present in the sample [29]. The peaks observed at 1562.71 cm⁻¹ corresponds to H-O-H bond and 1384.63 cm⁻¹ assigned to CH₃ bond.

From the fig 3, the absorption frequency bands are assigned at 3451.12, 2924.46, 2361.49, 1615.34, 1404.38, 1019.39, 808.20, 686.27, 537.26, 466.72 cm⁻¹. Probably, the absorption bands at 3.451.12 cm⁻¹ can be attributed to the OH bond. The band corresponds to 686.27 cm⁻¹ represents Cu. The band at 808.20 cm⁻¹ corresponds to CdO bond. The band at 466.72 cm⁻¹ corresponds to Ti-O bond. The band at 2924.46 cm⁻¹ represent C-H bond. The band at 1019.39 cm⁻¹ corresponds to C-O-C bond. Table 1 shows the FT-IR frequency of pure CdO-TiO₂ and Cu Doped CdO-TiO₂ nanostructure.

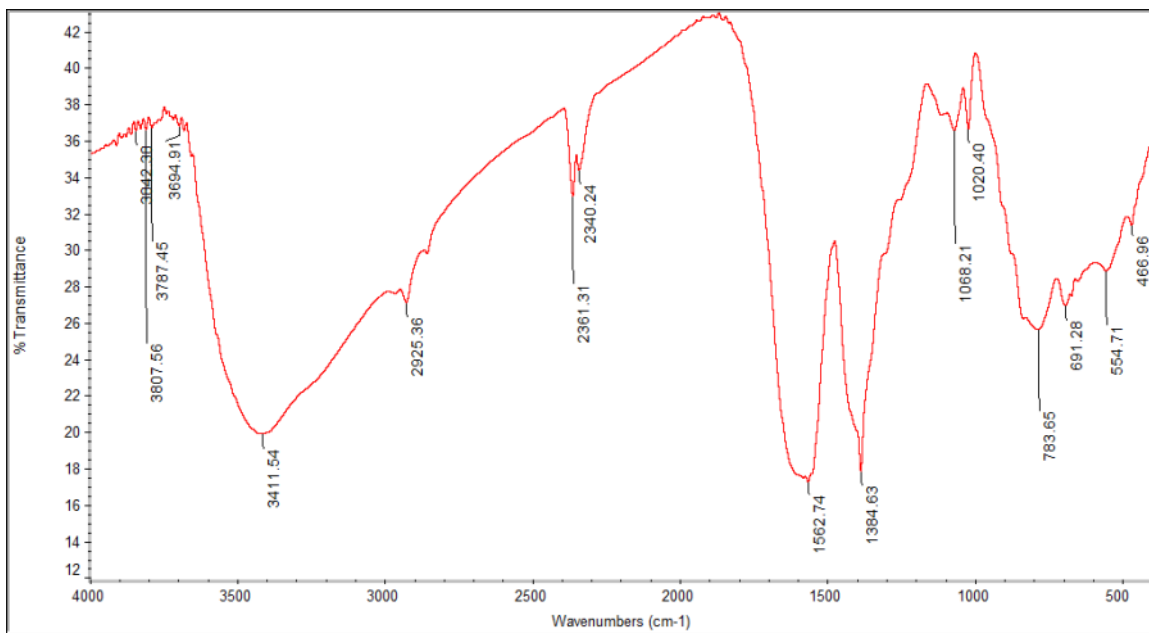


Figure 2 FT-IR spectrum of CdO-TiO₂ nanostructure

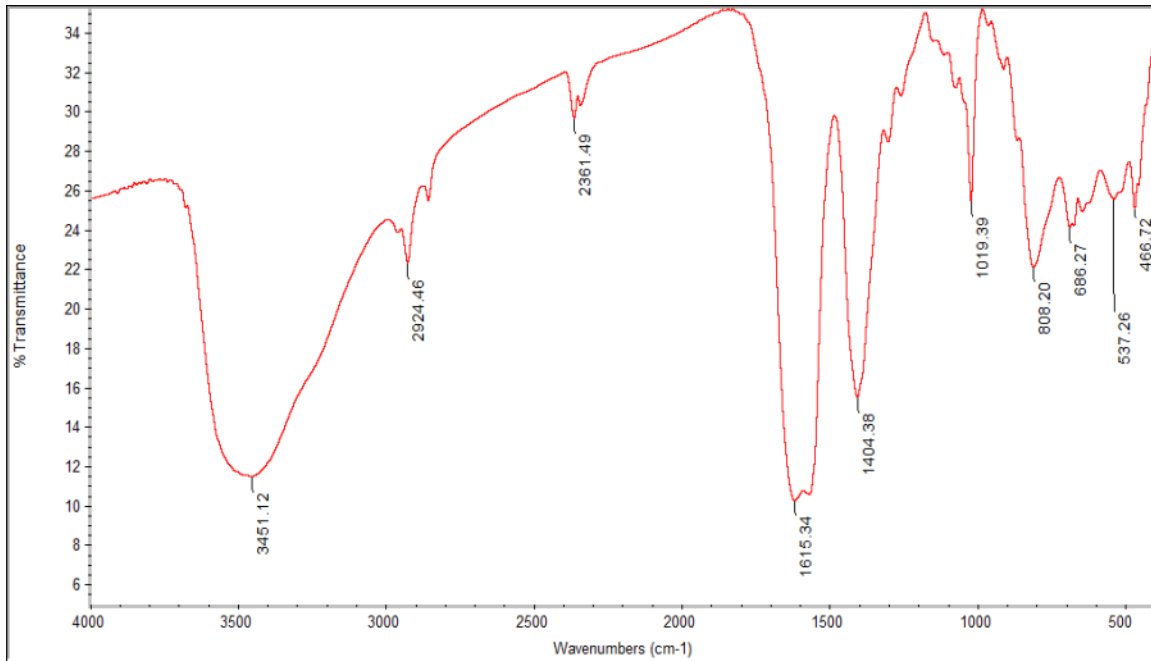


Figure 3 FT-IR spectrum of Cu doped CdO-TiO₂ nanostructure

Table 1: FT-IR Analysis of Pure CdO-TiO₂ and Cu Doped CdO-TiO₂ nanostructure

Frequency	Region	
	Pure CdO-TiO ₂	Cu doped CdO-TiO ₂
O-H bond	3411.54	3451.12
C-H bond	2926	2924.46
C-O-C bond	1068.21	1019.39
Ti-O bond	466.96	466.72
Cd-O bond	691.28	686.27
H-O-H bond	1562.71	1616.34
CH ₃ bond	1384.63	1404.38
Cu-O bond	-	686.27

3.3 Scanning Electron Microscope

The surface morphology of the synthesized Cu doped CdO-TiO₂ was studied using SEM. The SEM image of Cu doped CdO-TiO₂ shown in Fig 4. Fig 4 is the evident that the surface morphology of prepared Cu doped CdO-TiO₂ nanoparticles are plate-like nanostructure.

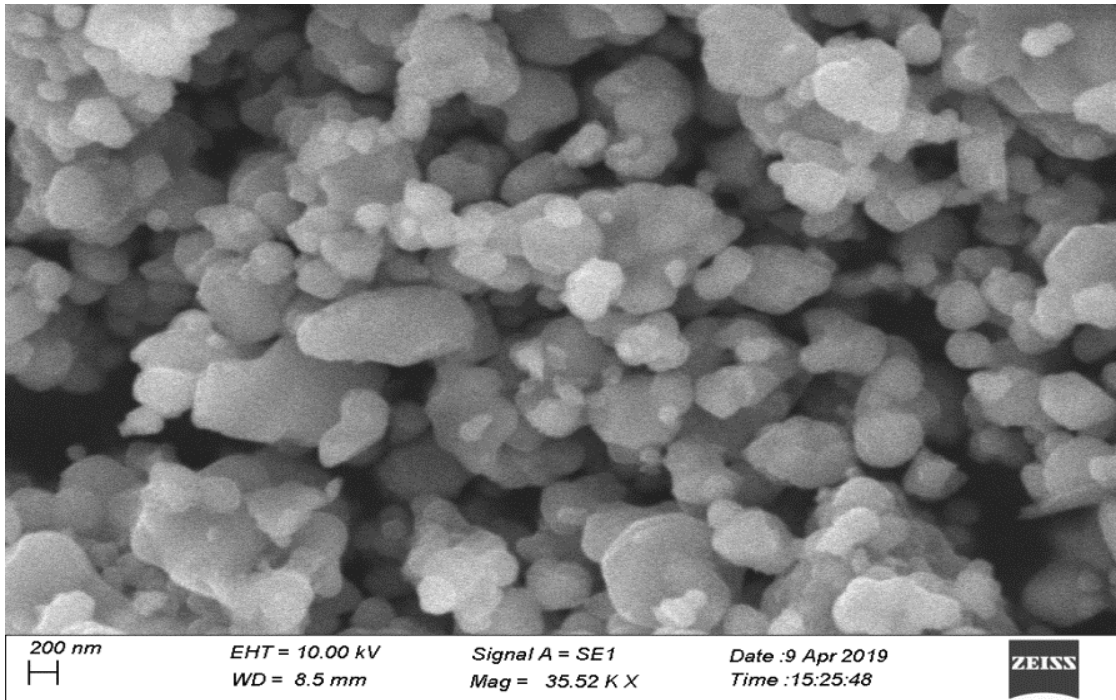


Figure 4 SEM image of Cu doped CdO-TiO₂ nanostructure

3.4 Particle Analysis

From this study, we determine the diameter of the Nanoparticles. The diameter of CdO-TiO₂ nanoparticles was 318nm. The diameter of the Cu doped CdO-TiO₂ nanoparticles was 598 nm. From this result we conclude that the prepared sample Nanometer in size.

3.5 Photocatalytic Activities

From the figures 5 and 6, we found that absorption peak decreases progressively in intensity with the light illumination time, indicating a decrease in the dye concentration in the solution.

The evaluation of the photocatalytic reaction was followed by an UV-Vis spectrometer, by periodically recording the absorption spectra in order to monitor the concentration change of the residual organic dye in the solution. The residual dye content in the solution was determined by a degradation percentage defined by the following relation.

$$X (\% \text{ degradation}) = (A_0 - A_t / A_0) * 100\%$$

Where A₀ is the initial dye absorbance, at maximum absorption wavelength of the dye, before illumination and A_t is the dye absorbance at time t.

From figure 7 (a,b), we conclude that the photodehydration rate of the dye increases with light irradiation time. Photodehydration rate of Cu doped CdO-TiO₂ nanoparticles was improved compared to CdO-TiO₂ Nanoparticles.

Here, when Cu doped CdO-TiO₂ nanoparticles irradiated using UV light with energy equal or greater than the band gap (2.5 eV), electrons are shifted from the valence band (VB) to the conduction band (CB) to turn over electron-positive hole (*e/h*) pairs. The valence band hole has positive sufficiency to generate hydroxyl radical ($\cdot\text{OH}$) at the TiO₂ surface [30]. Likewise, the conduction band electron has sufficient negative charge to deoxidize the O₂ molecules of solution, which successively directs to the propagation of additional series of OH radicals. These OH radicals having powerful and strong oxidizing agent, can lead to a partial or complete degrade the organic pollutants into less hazardous minerals, forming non-toxic products such as CO₂ and H₂O. The proposed mechanism is shown in Fig. 8, and chemical reaction that takes place at CdO photocatalyst surface is illustrated below

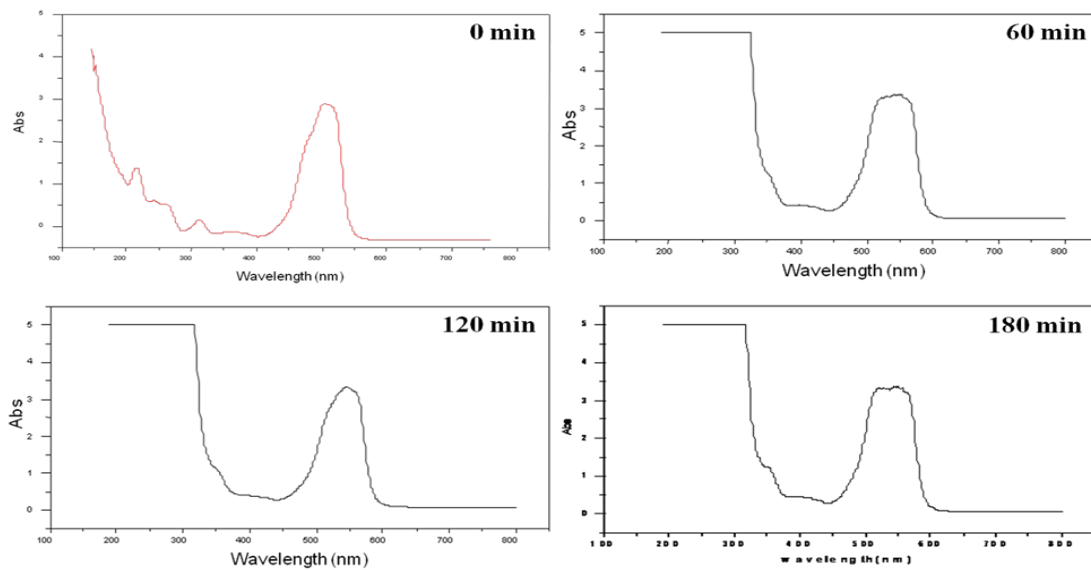
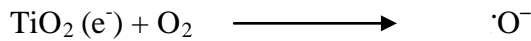
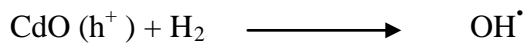
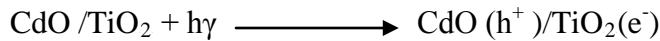


Figure 5 Photocatalysis for Pure CdO-TiO₂ nanostructure

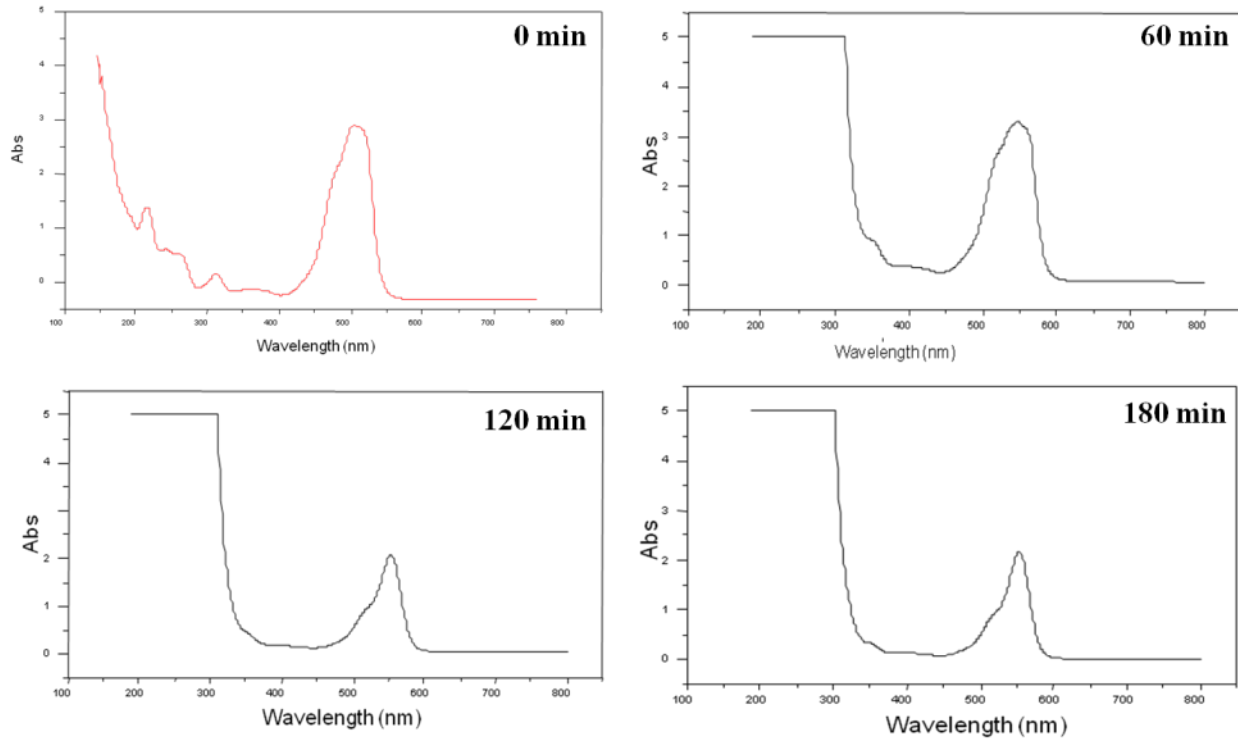


Figure 6 Photocatalysis for Cu doped CdO-TiO₂ nanostructure

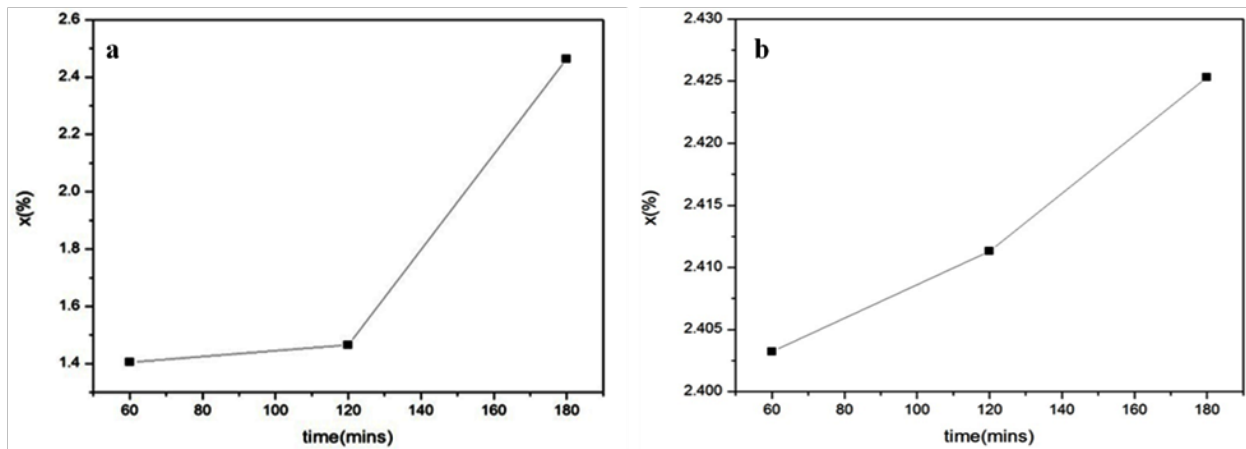


Figure 7 Photodegradation rate evaluation of Rhodamine B by the photocatalysis in the presence of (a) CdO-TiO₂ and (b) Cu doped CdO-TiO₂ nanostructure.

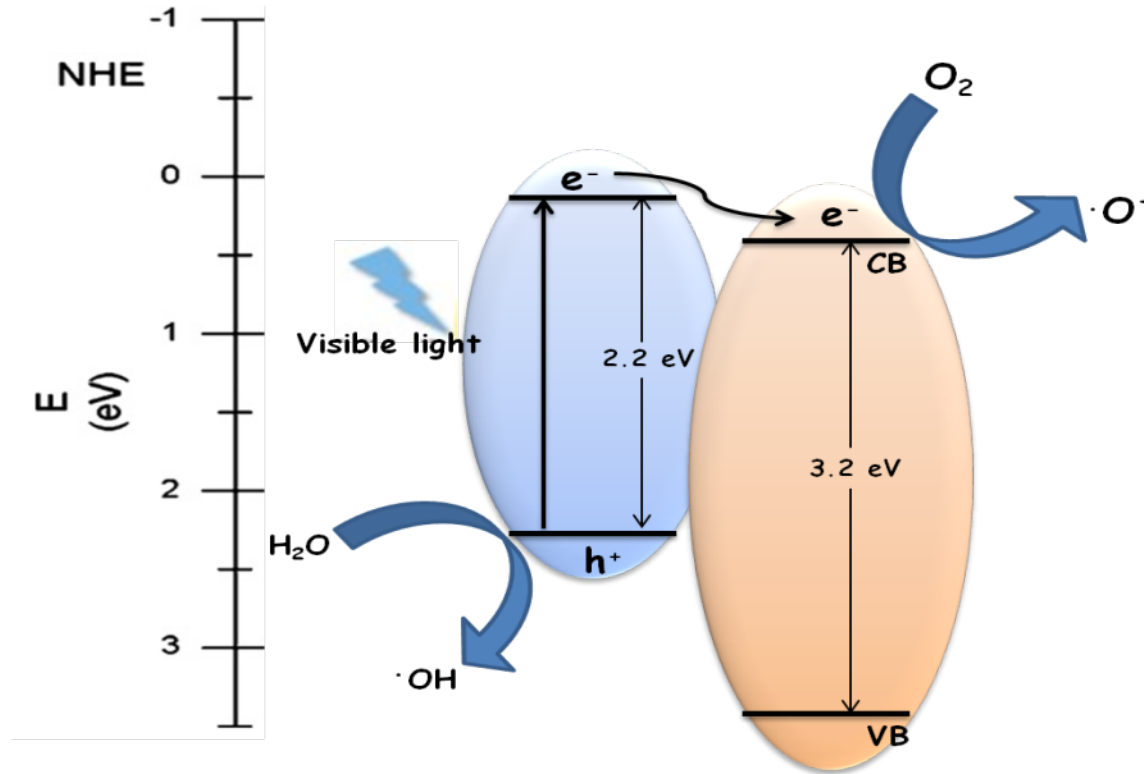


Figure 8 Schematic representation of photocatalytic mechanism

4. Conclusion

In this work, pure and Cu doped CdO-TiO₂ nanoparticles have been successfully prepared by chemical co-precipitation method. The prepared samples were subjected to various studies like UV analysis, FT-IR analysis, SEM analysis, Particle analysis and Photo catalytic analysis. The optical properties of the Cu doped CdO-TiO₂ nano particles are analyzed by UV-Vis spectroscopy and the band gap of the sample was found. Functional groups of the prepared sample are analyzed using FT-IR analysis. SEM pattern shows rod like particles of the Cu Doped Cdo-TiO₂ nanoparticles. From photocatalytic study, we determine the photocatalytic degradation rate of the dye increase with irradiation time. The diameter of the Cu doped CdO-TiO₂ nanoparticles were determined using particle analysis

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