

CdO-Fe₃O₄ nanocomposite with enhanced magnetic and photocatalytic properties

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Pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite were synthesized by a cost effective chemical method, and the samples were characterized by XRD, SEM, TEM, FT-IR, UV-Vis-NIR and PL. Also, magnetic and photocatalytic properties of the synthesized samples were studied. XRD patterns of the composite confirm the presence of diffraction peaks related to both CdO and Fe₃O₄. EDX spectrum confirms the presence of the elements Cd, O and Fe in the composite. Peaks related to Cd–O and Fe–O bonds were observed respectively at 688 cm⁻¹ and 592 cm⁻¹ in the FT-IR spectrum. The paramagnetic behavior of pure CdO becomes ferromagnetic when coupled with Fe₃O₄. The composite exhibited a high photodegradation efficiency of 92.85 % against the degradation of methylene blue dye under visible light radiation.

Keywords: nanocomposite; photoluminescence; ferromagnetism; photocatalytic

1. Introduction

Nanomaterials possess enhanced physicochemical, optical, mechanical and magnetic properties compared to those of bulk materials. In recent years, metal oxide semiconductor nanoparticles have attracted the attention of researchers due to their potential applications in several areas of physics, chemistry, biology and materials science [1]. Among the metal oxide semiconductors, cadmium oxide (CdO) is a II-VI group semiconductor which exhibits high electrical conductivity and optical transparency. Due to its narrow band gap of 2.42 eV between the Cd 5s-based conduction band and the O 2p-based valence band, CdO seems to be photoactive in nature [2]. In nanodimensions, CdO finds applications in solar cells, photodiodes, phototransistors, gas sensors, UV absorbers, oxygen storage materials and automobile exhaust catalysts [3]. Due to its high charge carrier mobility and favorable visible light absorption, CdO nanoparticles are used as photocatalyst for dye degradation [4]. Recently, it has been reported that CdO nanopowders

exhibited excellent antimicrobial activities [5]. However, regarding magnetic properties CdO is less studied metal oxide semiconductor due to its paramagnetic nature at room temperature [6]. The magnetic properties of CdO could be improved by doping it with magnetic metal ions or forming a composite mixture with ferromagnetic semiconductors. Iron oxide is a magnetic metal oxide semiconductor which finds applications in gas sensors, electrochemistry, pigments, drug carriers and waste water treatment [7]. Iron oxide exists in different forms such as hematite (α -Fe₂O₃), magnetite (Fe₃O₄), etc, depending upon the oxidation state of Fe. In hematite, Fe exists in 3+ oxidation state; whereas in magnetite it exists both in 2+ and 3+ states. In magnetite, the ferric ions are equally distributed between the tetrahedral and octahedral sites of the inverse spinel structure [8]. Due to its strong magnetic behavior, long durability, good biocompatibility, low toxicity, Fe₃O₄ nanoparticles are widely used in magnetic biomedicine, heavy metal ion removal, electromagnetic wave absorption, etc. [9-11]. This proves that Fe₃O₄ could be a good candidate for improving the optical, magnetic and catalytic properties of CdO. Therefore, in this work CdO-Fe₃O₄ nanocomposite was synthesized

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by a cost effective chemical method. Pure CdO nanopowder was also synthesized to stablish the improvement in its properties when coupled with Fe₃O₄. The synthesized samples were characterized by techniques such as XRD, SEM, TEM, UV-Vis-NIR, FT-IR and PL. The magnetic and photocatalytic properties were investigated and the obtained results are reported.

2. Materials and methods

Pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite were synthesized by a cost effective chemical method. Cadmium acetate $[Cd(CH_3COO)_2 \cdot 2H_2O]$ and ferric chloride [FeCl₃·6H₂O], each of analytical reagent grade with 99.9 % purity (Sigma make) were used as the precursor salts to synthesize the samples. To synthesize pure CdO nanopowders, 0.1 M of cadmium acetate was dissolved in aqueous solution (140 mL) and liquid ammonia (10 mL) mixture, stirred well for 2 h and kept undisturbed for 4 h. The obtained precipitate was cleaned with deionized water, calcined at 200 °C for 1 h and then crushed to get orange colored CdO nanopowder. CdO-Fe₃O₄ nanocomposite was synthesized by mixing the precipitates obtained earlier with the precipitates obtained by dissolving 0.1 M ferric chloride in a mixture of 140 mL deionized water and 10 mL liquid ammonia. The resultant components were calcined at 200 °C for 1 h and crushed to get CdO-Fe₃O₄ nanocomposite. The details regarding the instruments used to characterize the samples are compiled in Table 1.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the XRD patterns of (a) pure CdO nanopowder and (b) CdO-Fe₃O₄ nanocomposite.

3.1.1. Pure CdO

The XRD pattern of pure CdO (Fig. 1a) seems to be polycrystalline in nature with cubic crystal structure. The diffraction peaks in the XRD pattern were indexed to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes according to JCPDS card No.



Fig. 1. XRD patterns of (a) pure CdO nanopowder and (b) CdO-Fe3O4 nanocomposite.

73-2245. Pure CdO exhibits a strong (1 1 1) preferential growth which exactly matches with earlier reports [12, 13]. The crystallite size estimated using the Scherrer formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where β is the full width at half maximum value of the (1 1 1) peak, λ is the wavelength of the X-ray used (1.5406 Å) and θ is the Bragg angle), was found to be equal to 33.64 nm.

3.1.2. CdO-Fe₃O₄ composite

Peaks related to pure CdO (represented by * symbol) and peaks related to $(3\ 1\ 1)$, $(2\ 2\ 0)$, $(4\ 0\ 0)$ and $(4\ 4\ 0)$ planes of cubic Fe₃O₄ (JCPDS Card No. 79-0416) were observed in the XRD pattern of the composite (Fig. 1b). The presence of peaks related to CdO and Fe₃O₄ in the composite confirmed the formation of heterostructure between these two semiconductors. The average crystallite size of the composite calculated using β values of the (1 1 1) peak of CdO and (3 1 1) peak of Fe₃O₄ was found to be equal to 27.84 nm.

Structural studies	X-ray diffractometer (PRO analytical X ['] pert PRO with CuK α radiation X-ray source ($\lambda = 1.5406$ Å)		
Surface morphology	Scanning Electron microscope (HITACHI S-3000 H), Tecnai- 20G2 TEM instrument		
Functional group analysis	Perkin Elmer RX-1 FT-IR spectrophotometer		
PL studies	Varian Cary Eclipse fluorescence spectrophotometer		
Optical studies	UV-Vis-NIR double beam spectrophotometer (Lambda 35)		
Magnetic studies	Vibrating sample magnetometer (Lakshore 7401)		

Table 1. Instruments used to characterize the pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite.

3.2. Surface morphology and elemental analysis

Fig. 2 shows the SEM and TEM images and EDX spectra of a) pure CdO nanopowder and b) CdO-Fe₃O₄ nanocomposite, respectively.

SEM images confirm the presence of surface fully covered with grains. Nanosized grains with small pores are visible in the TEM image of pure CdO nanopowder; whereas for the composite, columnar and nanosized grains are visible. The elements Cd, Fe and O were observed in the EDX spectrum of the composite. The atomic percentage composition of Cd, Fe and O in the composite was found to be equal to 24.62, 30.96 and 44.42, respectively.

3.3. FT-IR studies

Fig. 3 shows the FT-IR spectrum of the CdO-Fe₃O₄ nanocomposite. The band observed at 3133 cm⁻¹ is attributed to the characteristic absorption of hydroxyls [14]. The peak at 2156 cm⁻¹ is probably due to the absorption of CO₂ from the ambient air atmosphere [15].

The peaks observed at 1732 cm^{-1} , 1620 cm^{-1} and 1402 cm^{-1} are assigned to the bending vibration of water molecules. The peak attributed to C=N stretching vibration is observed at 1658 cm^{-1} [16]. The absorption band at 1098 cm^{-1} corresponds to C–O band [17]. The peak attributed to Cd–O stretching vibration is observed at 688 cm^{-1} [18]. The peak related to Fe–O bond is observed at 592 cm⁻¹ [19]. The presence of peaks related to Cd–O and Fe–O bonds in the FT-IR spectrum strongly confirms the formation of composite involving the CdO and Fe_3O_4 semiconductors.

3.4. PL studies

Fig. 4 shows the room temperature PL spectrum of the CdO-Fe₃O₄ nanocomposite. The peaks at 433 nm, 462 nm and 533 nm are likely to have been originated from the oxygen vacancies [20].

The visible emission peak at 451 nm can be attributed to the structural defects or luminescent centres in the CdO-Fe₃O₄ nanocomposite. The blue emission peak at 485 nm originates from the electron transition from shallow donor level formed by Cd/Fe interstitials to shallow acceptor level formed by Cd/Fe vacancies. This is in accordance to Chen et al. [21] for Mg-doped ZnO thin films. The peak at 509 nm (2.44 eV) is related to the presence of Cd or Fe vacancies in the composite. The peak at 517 nm can be attributed to the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy on the surface of the composite. The peak at 525 nm is attributed to CdO which is attributed to deep trap emission that is less size dependent [22]. Defects related emission from the composite is observed at 576 nm. The vellow band emission at 588 nm might be due to the de-excitation of electrons via the surface/defect states present in the nanocrystals [23]. The peaks at 615 and 621 nm may be attributed to surface states which arise from the deep traps formed due to Fe vacancies [24].



Fig. 2. SEM, TEM images and EDX spectra of (a) pure CdO and (b) CdO-Fe3O4 nanocomposite.



Fig. 3. FT-IR spectrum of the CdO-Fe₃O₄ nanocomposite.



Fig. 4. PL spectrum of the CdO-Fe₃O₄ nanocomposite.

3.5. Optical studies

Fig. 5 shows the absorption spectra of pure CdO nanopowders and CdO-Fe₃O₄ nanocomposite. It can be seen that the absorbance decreases with the increase in wavelength for both the samples.

Absorption edges were observed at 502 nm and 456 nm, respectively in the spectra of pure CdO

nanopowder and CdO-Fe₃O₄ nanocomposite. Using the relation $E_g = 1240/ \lambda_{max}$ (where E_g is the optical band gap and λ_{max} is the absorption edge of the samples), the band gap values of pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite were estimated. The E_g values of CdO nanopowder and CdO-Fe₃O₄ nanocomposite were found to be equal to 2.47 eV and 2.72 eV, respectively.



3.6. Magnetic studies

The M-H plots (Fig. 6a) confirm that the paramagnetic nature of pure CdO nanopowder became ferromagnetic when coupled with Fe₃O₄. The ferromagnetic orderings observed for the composite may be related to defects and the valency change of Fe ions. Among the surface defects, oxygen vacancies play a vital role in inducing ferromagnetism in the composite. Each oxygen vacancy V_o introduces a large sized localized orbital and two unpaired electrons which would hop between the Fe^{2+} and Fe^{3+} ions via the V_o orbitals, which makes the Fe ions at the interface connected via the V_0 orbitals to align ferromagnetically. This is in accordance to the results reported by Gao et al. [25] for CuO/Cu₂O composites. The occurrence of ferromagnetism in composite materials can also discussed on the basis of mean field theory, RKKY interactions, carrier mediated mechanism and polaron percolation theory [26]. The role of electrons, oxygen vacancies and Fe ions in inducing ferromagnetism in the composite could be explained by the indirect double-exchange mechanism [27]. Decreased particle size also might have played a significant role in inducing ferromagnetic behavior in the CdO-Fe₃O₄ composite as reported by Tiwari et al. [28].

Fig. 6b shows the temperature dependent magnetization curves of the CdO-Fe₃O₄ nanocomposite measured in the zero field cooled (ZFC) and field cooled (FC) conditions, under an applied magnetic field of 25 Oe and in the temperature range of 5 K to 300 K, The magnetization exhibited a slow increase with decreasing temperature from 300 K to 25 K, followed by an abrupt increase upon further cooling. The blocking temperature of the CdO-Fe₃O₄ nanocomposite was found to be equal to 47 K.

3.7. Photocatalytic activity

The photocatalytic activities of pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite were tested against the degradation of methylene blue dye under visible light irradiation. To investigate the photocatalytic activity, 6 mg of CdO and CdO-Fe₃O₄ photocatalyst was dispersed in 100 mL aqueous solution containing 0.025 M of MB dye. Adsorption/desorption equilibrium was achieved by stirring the dye solution with the photocatalysts for 1 h in dark and irradiated with 100 W incandescent lamp. Fig. 7 shows the effect of irradiation duration on the intensity of the absorption of removed solution at different time intervals (0 min, 30 min, 60 min, 90 min, 120 min and 150 min), from which it can be seen that the absorbance at $\lambda = 600$ nm gradually decreases with an increase in irradiation time.

The photocatalytic efficiency values of the pure CdO and CdO-Fe₃O₄ photocatalysts (Table 2) were calculated using the relation:

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100 \tag{2}$$

where C_0 is the concentration before illumination and C is the concentration after light irradiation.

The photodegradation efficiency of the composite (92.85 %) was found to be higher than that of pure CdO nanopowder (82.35 %) after 150 min light irradiation. This can be attributed to the large specific surface area, decreased crystallite size and the more effective electron/hole pair separation. Based on the band gap, conduction band and valence band in CdO and Fe₃O₄ follow the band disposition of the composite which promotes the separation and transportation of photoinduced charge carriers causing an enhancement in





Fig. 6. (a) M-H and (b) M-T plots of CdO and CdO-Fe₃O₄ nanocomposite.



Fig. 7. Absorbance spectra of a) CdO nanopowder and b) CdO-Fe₃O₄ nanocomposite as a function of irradiation time.

its photocatalytic activity. Similar improved photocatalytic activity has been reported by Suganya et al. [29] for PbS-SnO₂ nanocomposite. The mechanism behind the photocatalytic activity of CdO-Fe₃O₄ nanocomposite is as follows:

Under visible light irradiation, e^{-}/h^{+} pairs are produced from the CdO-Fe₃O₄ photocatalyst according to the equation:

$$CdO - Fe_3O_4 + h\upsilon \rightarrow e^- + h^+$$

The photogenerated electrons are captured by the soluble O_2 to form superoxide radicals according to the equation:

$$e^- + O_2 \rightarrow O_2^*$$

The photogenerated holes left in the valence band are trapped by the surface hydroxyl forming hydroxyl radicals:

$$OH^- + h^+ \rightarrow OH^*$$

The holes also react with adsorbed H_2O to form hydroxyl radicals according to the equation:

$$H_2O + h^+ \rightarrow OH^* + H^+$$

The superoxide radicals get converted to H_2O_2 according to the equation:

$$O_2^*+~2H^+
ightarrow 2e^-
ightarrow H_2O_2$$

The final product of the reduction is also OH^{*} radicals according to the equation:

$$2O_2^{*-}+2H^+ \rightarrow 2OH^*$$

Photocatalyst	Irradiation time					
	30 min	60 min	90 min	120 min	150 min	
CdO	17.65	25.49	56.86	74.51	82.35	
CdO-Fe ₃ O ₄	28.57	35.71	67.86	82.14	92.85	

Table 2. Photocatalytic degradation efficiency of pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite in percentage.

The hydroxyl radicals along with superoxide radical anions effectively degrade the MB molecules according to the equation:

$$OH^* + O_2^{*-} + MB \rightarrow CO_2 + H_2O$$

(degradation of MB molecules)

Similar mechanism has been reported by Li et al [30] for Cu₂O/Fe₃O₄ composite photocatalysts.

4. Conclusion

Pure CdO nanopowder and CdO-Fe₃O₄ nanocomposite were successfully synthesized by a simple cost-effective chemical route. Polycrystalline nature was observed for both the pure CdO nanopowder and CdO-Fe₃O₄ composite. Decreased crystallite size was observed in the composite. Nanosized grains were observed from the TEM images of the synthesized samples. Peaks related to Cd-O and Fe-O occurred in the FT-IR spectrum of the composite. Ferromagnetic behavior with well-defined hysteresis loop was observed for the composite. The composite exhibited enhanced photocatalytic efficiency. From the obtained results it can be concluded that CdO-Fe₃O₄ nanocomposite is well suited for biomedical applications.

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