

Research Article

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Synthesis, Characterization and Study of Photocatalytic Activity of Cadmium Magnesium Nano Ferrites

Wasim Ullah Marwat*

Research Scholar, University of Peshawar, Pakistan

Abstract

To the best of our knowledge, there are no reports has been cited in the literature on the photo catalytic properties of Cd_vMg_{1v}Fe₂O₄ ferrite nanoparticles under solar light irradiation to till date. Considering the importance of Cd_vMg_{1v} Fe_2O_4 nanoparticles and their wide applications, we made an attempt to synthesize $Cd_xMg_{1x}Fe_2O_4$ (x=0.3,0.5,0.7,1.0) nañoparticles by co-precipitation method at 80°C then filtered and washed with distilled water. After drying, heat treatment was carried out for 3 hours at 600°C. The prepared samples were characterized using XRD (X-ray Diffraction Spectroscopy), SEM (Scanning Electron Microscopy), FT-IR (Fourier Transform Infra-Red Spectroscopy) and DSC (Differential Scanning Calorimetric) methods. The XRD result shows that all prepared samples crystallite size are in the range of 28 nm to 58 nm and lattice constant in the range of 8.41 to 8.68 nm. Scanning Electron Microscopy result shows that all the samples are spherical almost uniform in shape and the crystal size below 50 nm. XEDS result shows that the main components of the prepared samples are Cd, Mg, Fe and Oxygen. Fourier Transform Infra Red Spectroscopy results clearly indicate the Cd-Mg nano Ferrite are synthesized. Differential scanning calorimeter graphs shows the phase formation of all the samples. Band gap energy of the synthesized samples is calculated using the general equation E=mc² and found 2.95 -3.21 eV through Ultra Violet-Visible Spectrophotometer absorption studies. The photo catalytic property of Cd_yMg_{1.y}Fe₂O₄ nanoparticles was calculated during the Methyl Orange degradation with different time interval under solar light irradiation and found that Cd0,5Mg0,Fe2O4 having good Photocatalytic properties for Methyl Orange degradation.

Keywords: Photocatalytic activity; Nanoparticles; SEM; XRD

Introduction

A ferrite is a chemical compound of ceramic materials with iron (III) oxide (Fe_2O_3) as its main component. Ferrites are usually nonconductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite (Fe_2O_3) or magnetite (Fe_3O_4) as well as oxides of other metals. Ferrites are, like most other ceramics, hard and brittle.

Semiconductor oxides are important for many environmental and energy issues because, they cannot only utilize solar energy to eliminate harmful pollutants present in air and water but also effectively detect toxic and hazardous gases as well as biological species [1,2].

The consumption of non-renewable energy sources such as fossil fuels is less favorable nowadays, not only because of current shortage and a final exhaustion of these sources but also for serious environmental considerations [3,4].

The conversion of solar energy (electromagnetic radiation) into a practically applicable form can be achieved by a photo catalyst (i.e. semiconductor with an appropriate band gap and band edges) through a process that is similar to photosynthesis [4,5].

After studying the above mentioned literature of different ferrites and metal oxide photocatalytic degradation properties, we have synthesized the Cd-Mg Ferrites to determine its organo pollutant Methyl Orange photo catalytic degradation. Cd-Mg Ferrite is synthesized by co-precipitation method and heat treated to 600°C for phase formation and then characterize by XRD, SEM, FTIR and DSC. After confirmation from their characterization, their band gap energy is determined by using UV-Visible Spectrophotometer and then Photocatalytic properties in the presence of sunlight by degradation of Methyl Orange.

Materials and Method

Chemicals used

During synthesis of $Cd_xMg_{1-x}Fe_2O_4$, following chemicals were used without further purification:

- a. Analytical grade nitrates of Cd and Mg
- b. Analytical grade Iron Sulphate hepta hydrate
- c. Analytical grade Sodium Hydroxide
- d. De-ionized water of very low conductivity

Co-precipitation method

Chemical methods for the synthesis of are believed to be better than the physical methods because chemical reaction take place at molecular level. Because of this reason shape, size and morphology of the nanoparticles can be controlled in a better way. In this work I followed [6,7] a chemical method Co-precipitation for the synthesis of Cd₂Mg_{1,2}Fe₂O₄ nanoparticles, which is explained below.

• Stoichiometric quantity of metal salts solution was prepared separately in de-ionized water. These solutions then mixed together and heated to 80°C with continuous stirring.

*Corresponding author: Wasim ullah Marwat, Research Scholar, University of Peshawar, Pakistan, Tel: 3193- 9218491; E-mail: wasimsaha@gmail.com

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- 2 M NaOH solution was prepared separately and heated to 80°C.
- Then poured the NaOH solution into the metal salt solution with continuous stirring and heated for 45 mints, after 45 mints the heating is stopped but stirring continue till the mixture temperature reached to room temperature, then filter the solution through wattman filter and precipitate washed with de-ionized water till pH reached to 7. These precipitates were dried in oven for two hours at 120°C. After drying each sample heat treated in furnace for 3 hours at 600°C.

Results and Discussion

XRD analysis

To evaluate the crystal structure of $Cd_xMg_{1-x}Fe_2O_4$ analysis were carried out and the XRD images of the samples are presented in Figure 1.

The diffraction pattern analysis by using (220), (311), (400), (422), (104), (440), (110), (024), (116) and (300) reflection planes confirms the cubic spinel structures. The peaks position and relative intensity matches with the standard MgFe₂O₄ and CdFe₂O₄ powder diffraction data (JCPDC card #17-0464 and JCPDC card # 22-1063). This shows that synthesized Cd_xMg_{1-x}Fe₂O₄ samples belongs to space group Fd3m(227) cubic spinel structure. To calculate the crystallite size (D) of Cd_xMg_{1-x}Fe₂O₄ by using Full width at half max (FWHM) of XRD peaks through Scherer's relation.

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

 β is the broadening of the diffraction line measured at half maximum intensity (radians) and λ =1.5406 A° , the wavelength of

Cu-Ka. The average crystallite sizes of $Cd_xMg_{1,x}Fe_2O_4$ were found by calculation 28 nm, 43 nm, 45 nm and 58 nm. The lattice constant (α) of the

 $\rm Cd_x Mg_{1-x} Fe_2 O_4$ nanostructures were determined using the following relationship.

$$\alpha = d_{hkl} \sqrt{(h^2 + k^2 + l^2)}$$
⁽²⁾

The lattice parameter α varies with Cd²⁺concentration. It was observed that the lattice parameter increases linearly with concentration of Cd²⁺. The calculated lattice parameters α for MgFe₂O₄ and CdFe₂O₄ samples were found to be in the range from 0.854 nm to 0.869 nm, respectively, which are in good agreement with the literature values of 0.838 and 0.869 nm for MgFe₂O₄ and CdFe₂O₄ samples. The larger value of lattice parameter α , for CdFe₂O₄ compared to MgFe₂O₄ is due to the larger ionic radius of Cd²⁺ than Mg²⁺. The calculated density of CdFe₂O₄ is greater than Cd₂Mg_{1,2}Fe₂O₄ (Table 1)

SEM analysis

The scanning electron microscopy studies were undertaken for the samples of $Cd_xMg_{1-x}Fe_2O_4$ and images are shown in Figure 2. It is evident from the SEM micrographs that these samples have uniform, almost spherical structural, morphology with a narrow size distribution of the particles. The particle size of these nano ferrites are in the range from 20 nm to 40 nm.

FT-IR

FTIR spectra were recorded in the range of 400–4000 cm⁻¹ as shown in the Figures 3a-3d. The IR bands of solids are usually assigned to the vibrations of ions in the crystal lattice. Two main broad metal-oxygen bands are seen in the FTIR spectra of all ferrites in particular.



S.No	Sample ID	Lattice Constant (A ^o)	Crystallite Size (nm)	Calculated Density (g/cm ²)
1	Cd _{0.7} Mg _{0.3} Fe ₂ O ₄	8.54	58	5.37
2	Cd _{0.5} Mg _{0.5} Fe ₂ O ₄	8.46	45	5.27
3	Cd _{0.3} Mg _{0.7} Fe ₂ O ₄	8.41	43	5.25
4	CdFe ₂ O ₄	8.69	28	5.50

Table 1: Calculated density of $CdFe_2O_4$ is greater than $Cd_xMg_{1,x}Fe_2O_4$.

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Below 700 cm⁻¹ the octahedral-metal stretching vibration frequency (Oh) $M_{octa} \leftrightarrow O$ [B site] and 800-900 cm⁻¹ corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site (Td) M_{tetra} $\leftrightarrow O$ [A site], The FTIR spectrum of nano crystalline Cd-Mg ferrite is shown in Figures 4a-4d. In the FTIR spectrum of the samples, the band appears from 1098-1120 cm⁻¹, which relates to lattice vibration of oxide ion against the cations. The bands in the region from 1300-1700 cm⁻¹ are relates to both Symmetric & asymmetric C-O stretching frequency, and this may be due to the CO_2 adsorbed by the samples from atmosphere.

The Octahedral Stretching vibration frequency of CdFe₂O₄ is 623



Figure 3c: FTIR Spectra of Cd_{0.5}Mg_{0.5}Fe₂O₄.

cm⁻¹, Cd_{0.3}Mg_{0.7}Fe₂O₄ is 615 cm⁻¹, Cd_{0.5}Mg_{0.5}Fe₂O₄ is 625 cm⁻¹ show that as the Cd concentration increases the absorption bands value increases but as the Cd value reaches to a max value the absorption band value decreases i.e. Cd_{0.7}Mg_{0.3}Fe₂O₄ absorption band value is 602 cm⁻¹.

Similarly the lattice vibration of oxide against to metal absorption band in $CdFe_2O_4$ is 1120 cm⁻¹ as the Cd concentration increases these value decreases and in $Cd_{0.7}Mg_{0.3}Fe_2O_4$ there is no lattice vibration of oxide to metal. This FTIR spectrum results are quite similar to that given in the literature.

DSC: differential scanning calorimeter

The DSC (Differential Scanning Calorimetric) curves observed for

dried samples at 120°C and heat treated samples at 600°C of $Cd_xMg_{1-x}Fe_2O_4$ in the temperature range 25-600°C at the heating rate of 10°C/ min shown in Figures 4a-4d.

The dried samples peaks at 120°C, show low endothermic peaks near about100°C, with different peak width, grater the peak width greater amount of water is evolving, smaller the peak width less amount of water is present which is evolving from the surface, except $CdFe_2O_4$ and many other small endothermic peaks show while heat treated samples at 600°C show one endothermic peak near about 235-250°C showing the trapped water removal, while no other endothermic or exothermic peaks are observed but show straight line in ascending mode., Which

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describes that the phase already formed and no decomposition or formation takes place.

Optical studies

To determine the Band gap energy by using the UV-Visible Spectrophotometer (UV-1800 Shimadzu Japan), the samples first

dispersed in ethanol, by using the Sonicator for 10 minutes then each sample run on UV-Visible Spectrophotometer in the range from 200 nm to 800 nm to determine the cut off wavelength by using the ethanol as a reference in the Scan measure mode as shown in the Figures 5a-5d.

By putting the value of cut off wavelength of each sample in the general equation $E{=}hc/\lambda,$ band gap energy is determined

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Where,

E is the band gap energy in electron volt (eV)

h is plank constant equal to 6.626×10^{-34} Joule Second

C is constant (speed of light 3×10^8 m/s)

 λ is the cut off wavelength and

 $1 \text{ ev} = 1.6 \times 10^{-19} \text{ joule}$

From above equation the band gape energy is determined of each sample as represented in the Table 2.

MO degradation

To examine the photocatalytic degradation properties of the $Cd_xMg_{1,x}Fe_2O_4$, we have selected the Methyl Orange which is one of the great Organic pollutants of dyes industries and not easily degraded, therefore we added 0.05 g of each nano ferrite samples in 50 ml of 10











S.NO	Sample ID	Cut Off Wavelength (nm)	h (joule Sec)	C (m/Sec)	Formula	Band Gap Energy (eV)
01	CdFe ₂ O ₄	398	6.626×10 ⁻³⁴	3×10 ⁸	E=hc/λ	3.12
02	Cd _{0.7} Mg _{0.3} Fe ₂ O ₄	404	6.626×10 ⁻³⁴	3×10 ⁸	E=hc/λ	3.07
03	Cd _{0.5} Mg _{0.5} Fe ₂ O ₄	420	6.626×10 ⁻³⁴	3×10 ⁸	E=hc/λ	2.95
04	Cd _{0.3} Mg _{0.7} Fe ₂ O ₄	386	6.626×10 ⁻³⁴	3×10 ⁸	E=hc/λ	3.21

Table 2: Band gap energy of Cd_xMg_{1,x}Fe₂O₄.

S.No	Time(min)	Sample ID/MO Conc.				
		CdFe ₂ O ₄	Cd _{0.7} Mg _{0.3} Fe ₂ O ₄	Cd _{0.5} Mg _{0.5} Fe₂O₄	Cd _{0.3} Mg _{0.7} Fe ₂ O ₄	
01	30	8.55	8.927	4.012	8.932	
02	60	7.652	6.589	3.166	7.357	
03	90	6.156	5.29	2.349	5.80	

Table 3: Methyl Orange Degradation Table (MO Conc.10 ppm).

ppm of MO solution and stayed the each sample in dark for 30 minutes for equilibrium adsorption/desorption then sonicate for 10 minutes at ambient temperature and placed in sunlight at room temperature with continuous stirring then after different intervals of time the samples is centrifuged and determine the concentration of MO of each added sample against the calibration curve of 10 ppm of MO. The data is tabulated in the Table 3 and as a graphically shown in Figure 6.

Conclusion

Photocatalytic activity of Co-precipitation synthesized $Cd_xMg_{1.x}Fe_2O_4$ was evaluated by photocatalytic decomposition/degradation of MO in aqueous solution at room temperature. 0.05 g of each samples were placed into the 50 ml volumetric flask containing 50 mL of 10 ppm of MO aqueous solutions and mixed by ultrasonication for 10 min. Subsequently, the mixture was stirred in dark to obtain adsorption/desorption equilibrium. Through UV-Vis Spectro

photometer, then after different intervals of time the specific volume of samples is separated from the mother solution of each Cd_xMg_{1,x} Fe₂O₄ sample and centrifuged and then run against the standard curve and determined its concentration as illustrated in Figure 6 and Table 3. The result shows that with the passage of time the concentration of methyl orange is decreases as tabulated in graph. These results confirm that the effective degradation of the MO occurs only in the presence of Cd_xMg_{1x}Fe₂O₄ and sunlight irradiation, and this is the first time we are reporting Cd_xMg_{1-x}Fe₂O₄ as a new photo catalyst to degrade MO organic contaminant. The average particle size of $Cd_xMg_{1-x}Fe_2O_4$ is 35 nm was synthesized by co-precipitation process, and the formation of Cd_vMg_{1-v} Fe₂O₄ was confirmed through XRD, SEM, FTIR and DSC. The band gap energy of each sample is determined by using UV-Vis Spectrophotometer. Photocatalytic activity of Cd_xMg_{1,x}Fe₂O₄ was evaluated on Methyl Orange degradation under sunlight and found to be effective on degrading the methyl orange at room temperature.

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