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

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Abstract

To the best of our knowledge, there are no reports has been cited in the literature on the photo catalytic properties of Cd Mg \_x \_Fe _2 O_4 ferrite nanoparticles under solar light irradiation to till date. Considering the importance of Cd Mg \_x \_Fe _2 O_4 nanoparticles and their wide applications, we made an attempt to synthesize Cd Mg \_x \_Fe _2 O_4 (x=0.3, 0.5, 0.7, 1.0) nanoparticles 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 $E=mc^2$ and found 2.95 - 3.21 eV through Ultra Violet-Visible Spectrophotometer absorption studies. The photo catalytic property of Cd Mg \_x \_Fe _2 O_4 nanoparticles was calculated during the Methyl Orange degradation with different time interval under solar light irradiation and found that Cd Mg \_0.5 \_Fe _2 O_4 having good Photocatalytic properties for Methyl Orange degradation.

Keywords: Photocatalytic activity; Nanoparticles; SEM; XRD

Materials and Method

Chemicals used

During synthesis of Cd Mg \_x \_Fe _2 O_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 Cd Mg \_x \_Fe _2 O_4 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.

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Received October 24, 2014; Accepted November 27, 2014; Published December 04, 2014

Citation: Marwat WU (2014) Synthesis, Characterization and Study of Photocatalytic Activity of Cadmium Magnesium Nano Ferrites. J Material Sci Eng 3: 145. doi:10.4172/2169-0022.1000145

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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\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{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 MgFe\textsubscript{2}O\textsubscript{4} and CdFe\textsubscript{2}O\textsubscript{4} powder diffraction data (JCPDC card #17-0464 and JCPDC card # 22-1063). This shows that synthesized Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} samples belongs to space group Fd\textsubscript{3}m(227) cubic spinel structure. To calculate the crystallite size (D) of Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} by using Full width at half max (FWHM) of XRD peaks through Scherer’s relation.

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

\( \beta \) is the broadening of the diffraction line measured at half maximum intensity (radians) and \( \lambda = 1.5406 \text{ Å} \), the wavelength of Cu-Ka. The average crystallite sizes of Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} were found by calculation 28 nm, 43 nm, 45 nm and 58 nm. The lattice constant (\( a \)) of the Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} nanostructures were determined using the following relationship.

\[ a = \frac{d_{hkl}}{\sqrt{h^2 + k^2 + l^2}} \]  

The lattice parameter \( a \) varies with Cd\textsuperscript{2+} concentration. It was observed that the lattice parameter increases linearly with concentration of Cd\textsuperscript{2+}. The calculated lattice parameters \( a \) for MgFe\textsubscript{2}O\textsubscript{4} and CdFe\textsubscript{2}O\textsubscript{4} 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 MgFe\textsubscript{2}O\textsubscript{4} and CdFe\textsubscript{2}O\textsubscript{4} samples. The larger value of lattice parameter \( a \) for CdFe\textsubscript{2}O\textsubscript{4} compared to MgFe\textsubscript{2}O\textsubscript{4} is due to the larger ionic radius of Cd\textsuperscript{2+} than Mg\textsuperscript{2+}. The calculated density of CdFe\textsubscript{2}O\textsubscript{4} is greater than Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{4} (Table 1).

SEM analysis

The scanning electron microscopy studies were undertaken for the samples of Cd\textsubscript{x}Mg\textsubscript{1-x}Fe\textsubscript{2}O\textsubscript{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\textsuperscript{-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.
Below 700 cm\(^{-1}\) the octahedral-metal stretching vibration frequency (\(\text{Oh}) \ M_{\text{octa}} \leftrightarrow O \ [B \ site]\) and 800-900 cm\(^{-1}\) corresponds to intrinsic stretching vibrations of the metal at the tetrahedral site (Td) \(\ M_{\text{tetra}} \leftrightarrow O \ [A \ site]\). 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 CdFe\(_2\)O\(_4\) is 623...
cm⁻¹, Cd₀.₃Mg₀.₇Fe₂O₄ is 615 cm⁻¹, Cd₀.₅Mg₀.₅Fe₂O₄ 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. Cd₀.₇Mg₀.₃Fe₂O₄ absorption band value is 602 cm⁻¹.

Similarly the lattice vibration of oxide against to metal absorption band in CdFe₂O₄ is 1120 cm⁻¹ as the Cd concentration increases these value decreases and in Cd₀.₇Mg₀.₃Fe₂O₄ 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 CdₓMg₁-xFe₂O₄ 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 CdFe₂O₄ 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
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.
Where,

- $E$ is the band gap energy in electron volt (eV)
- $h$ is plank constant equal to $6.626 \times 10^{-34}$ Joule Second
- $C$ is constant (speed of light $3 \times 10^8$ m/s)
- $\lambda$ is the cut off wavelength and $1 \text{ev} = 1.6 \times 10^{-19}$ Joule

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

**MO degradation**

To examine the photocatalytic degradation properties of the $\text{Cd}_x\text{Mg}_{1-x}\text{Fe}_2\text{O}_4$, 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

![Figure 4b: DSC graph of Cd$_{0.3}$Mg$_{0.7}$Fe$_2$O$_4$.](image)

![Figure 4c: DSC graph of Cd$_{0.5}$Mg$_{0.5}$Fe$_2$O$_4$.](image)
Figure 4d: DSC graph of Cd$_{0.7}$Mg$_{0.3}$Fe$_2$O$_4$.

Figure 5a: CdFe$_2$O$_4$ Band Gap energy graph.

Figure 5b: Cd$_{1-x}$Mg$_x$Fe$_2$O$_4$ Band Gap energy graph.
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 was 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 CdxMg1-xFe2O4 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 Spectrophotometer, then after different intervals of time the specific volume of samples is separated from the mother solution of each CdxMg1-xFe2O4 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 CdxMg1-xFe2O4 and sunlight irradiation, and this is the first time we are reporting CdxMg1-xFe2O4 as a new photo catalyst to degrade MO organic contaminant. The average particle size of CdxMg1-xFe2O4 is 35 nm was synthesized by co-precipitation process, and the formation of CdxMg1-xFe2O4 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 CdxMg1-xFe2O4 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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**Table 2:** Band gap energy of CdxMg1-xFe2O4.

| S.No | Sample ID         | Cut Off Wavelength (nm) | \( h \) (Joule Sec) | \( C \) (m/Sec) | Formula   | Band Gap Energy (eV) |
|------|-------------------|-------------------------|---------------------|----------------|------------|---------------------|
| 01   | CdFe2O4           | 398                     | \( 6.626 \times 10^{-34} \) | \( 3 \times 10^8 \) | \( E=hc/\lambda \) | 3.12                |
| 02   | Cd0.7Mg0.3Fe2O4   | 404                     | \( 6.626 \times 10^{-34} \) | \( 3 \times 10^8 \) | \( E=hc/\lambda \) | 3.07                |
| 03   | Cd0.5Mg0.5Fe2O4   | 420                     | \( 6.626 \times 10^{-34} \) | \( 3 \times 10^8 \) | \( E=hc/\lambda \) | 2.95                |
| 04   | Cd0.3Mg0.7Fe2O4   | 386                     | \( 6.626 \times 10^{-34} \) | \( 3 \times 10^8 \) | \( E=hc/\lambda \) | 3.21                |

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

| S.No | Time(min) | CdFe2O4 | Cd0.7Mg0.3Fe2O4 | Cd0.5Mg0.5Fe2O4 | Cd0.3Mg0.7Fe2O4 |
|------|-----------|---------|----------------|----------------|----------------|
| 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           |
Figure 6: MO 10 ppm Degradation Curve.

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