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Optical and photocatalytic properties of CdFe₂O₄ nanocatalysts: Potential application in water treatment under solar light irradiation

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ABSTRACT

A solar light active $CdFe_2O_4$ photocatalyst was successfully prepared by sol-gel autocombustion method and annealed for 2 hours at different temperature. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) analyses were done to investigate the effect of calcination temperature on the particle size, formation of desired crystalline phase and removal of water and nitrate impurities. Scanning electron microscopy was used to analyze the morphology of the $CdFe_2O_4$ sample. The diffuse reflection spectra results show that $CdFe_2O_4$ photocatalyst can absorb visible light. The effect of calcination temperature on band gap energy was studied and the optical spectra indicate that the $CdFe_2O_4$ has a direct band gap due to direct transition. The photocatalytic activity of $CdFe_2O_4$ under solar light irradiation was evaluated by the degradation of methylene blue (MB) a model organic pollutant at different calcination temperatures. The photocatalytic experimental result demonstrates that $CdFe_2O_4$ sample calcined at $600^{\circ}C$ shows can effectively degrade the pollutant present in water. Recyclability experiment shows that $CdFe_2O_4$ calcined at $600^{\circ}C$ is more stable and recyclable photocatalyst under solar light.

Keywords: Sunlight, Photocatalytic activity, Ferrites, Optical properties, recyclability.

INTRODUCTION

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]. A vast clean energy source that remains incompletely exploited is solar energy. With an annual insolation level of 1000 W/m², solar energy is an attractive energy source that exceeds all current human needs [3,4]. The conversion of solar energy (electromagnetic radiation) into a practically applicable form can be achieved by a photocatalyst (i.e. semiconductor with an appropriate band gap and band edges) through a process that is similar to photosynthesis [4,8]. Many semiconductors have been investigated for the purpose of seeking potential photocatalysts, most of them suffer from their intrinsic limitations (band gap > 3.1 eV) that only ultraviolet radiation can be utilised, which makes up of about 3% of the whole solar irradiation [9,10] and ca. 46% visible light, indicating that low band gap catalysts are more desirable. In this respect, developing a photocatalyst that efficiently extends photocatalytic activity into visible spectral region remains a great challenge.

Use of the ecofriendly ferrites [11–14] for efficient solar energy usage has been an important topic in the visible light photocatalysis research. Ferrites are well known for their tremendous applications in the field of magnetic and electronic materials [15,16], but there are few reports on their photocatalyst applications [17,18]. Unlike TiO₂, the ferrites offer an advantage of displaying the desirable optical absorption for the low energy photons (hv ~ 2 eV), and of exhibiting the well suited electronic structure desirable for photocatalytic applications.

To make full use of solar energy, many attempts have been made to prepare the narrow band gap ferrite semiconducting material that utilizes the much larger visible region. Some of the recent reports can be important indicators with respect to the potential of visible light photocatalytic application of the spinel ferrites. For instance, Jang et al. [19] and Jung et al. [20] respectively demonstrated that $ZnFe_2O_4$ and $CaFe_2O_4$ systems are useful for solar photocatalytic degradation of pollutants. Similarly, in case of homo [21] or hetero [22] composite ferrite systems, $CaFe_2O_4:MgFe_2O_4$ and $ZnFe_2O_4:SrTiO_3$ have been shown to be efficient and useful for photocatalytic water splitting. It has been reported that Ching Cheng *et al* [23]. investigated the effects of cation distribution in $CdFe_2O_4$, M. Yokoyama *et al* [24]. studied the magnetic properties of cadmium ferrite prepared by coprecipitation, Ashok Gadkaria *et al* [25].reported on structural and magnetic properties of CuFe_2O_4 ferrites, silva o *et al*.[26] reported the magnetic resonance investigation of cadmium ferrite. To the best of our knowledge, as per the literature there are no reports has been cited in the literature on the photocatalytic properties of cadmium ferrite nanoparticles under solar light irradiation to till date.

Considering the importance of cadmium ferrite nanoparticles and their wide applications, we made an attempt to design the solar light active photocatalyst with optimizing the calcination temperature by sol-gel auto-combustion reaction method. UV-vis absorption studies of the samples were performed to investigate the photoabsorption properties and enabled us to calculate the band gap energy of the prepared photocatalyst. Methylene blue (MB) was selected as a model organic pollutant; the photocatalytic property of cadmium ferrite nanoparticles calcined at different temperature under solar light irradiation was investigated and reported.

MATERIALS AND METHODS

2.1 Catalyst preparation:

 $CdFe_2O_4$ compounds were synthesized by the sol–gel auto-combustion reaction method. The detailed process can be described as follows (Figure.1). The analytical grade $Fe(NO)_3 \cdot 9H_2O$, $Cd(NO)_3 \cdot 4H_2O$ and citric acid ($C_6H_8O_7 \cdot H_2O$) were used as raw materials. The stoichiometric amount of nitrates and citric acid was first dissolved in distilled water to form a clear solution. The molar ratio of nitrates to citric acid was 1 : 1. The solution was evaporated by intensive stirring and heating for 4 hours at 70 °C, heated to 90 °C and kept at this temperature until the sol turned into a transparent gel. The gel was then heated to experimentally determined temperature of 250 °C for 20 minutes, so that auto-combustion would take place. Finally, the product was calcined in a furnace for 2 hours at different temperatures.

2.2. Characterization techniques

The phase compositions and structures of the $CdFe_2O_4$ samples were determined by powder X-ray diffraction (PXRD, PANalytical Xpert Pro X-ray Diffractometer) with Cu-K α radiation (k = 0.15406 nm) over the 2 θ range of $10-80^{0}$. The morphology of CdFe₂O₄-ferrite samples was observed by scanning electronic microscopy (SEM) with a JSM-6700 LV electron microscope operating at 5.0 kV and the chemical compositions were examined by X-ray energy dispersive spectroscopy (XEDS). The structural characterization of the nanocrystalline CdFe₂O₄ samples were examined by Fourier transform infrared spectroscopy (FTIR) (using a Nicolet IR200 FT-IR spectrometer). Light absorption properties of the CdFe₂O₄ nanocrystals dispersed in ethylene glycol were studied by a UV–Vis spectrophotometer (Shimadzu, UV-1650 PL model).

2.3. Measurement of photocatalytic activity

Photocatalytic activities of the synthesized $CdFe_2O_4$ samples were measured under solar light irradiation by the decomposition of methylene blue (MB) in an aqueous solution at ambient temperature. In each experiment, 0.05g of $CdFe_2O_4$ nanoparticles were added into 50 ml of methylene blue solution with a concentration of 10 mg l⁻¹. The suspension was magnetically stirred in the dark for 30 min to establish the adsorption/desorption equilibrium at room temperature, then the solution was directly irradiated under solar light. During irradiation, stirring was maintained to keep the mixture in suspension. At regular intervals, samples were taken from the suspension and then magnetically separated to remove $CdFe_2O_4$ nanoparticle catalysts and reused for additional runs. The change in the

concentration of each degraded solution was monitored on a UV–Vis spectrophotometer (Shimadzu, UV-1650 PL model) by measuring the absorbance in the range of 200–800nm wavelength. Distilled water was used as the reference sample. In addition we investigated the recyclability of $CdFe_2O_4$, after each catalytic run, the sample was washed and dried to permit subsequent photoreaction cycles.



Fig. 1 Flow chart of sol-gel auto combustion process

RESULTS AND DISCUSSION

3.1 XRD and SEM analysis

A structural characterization of synthesized samples were carried out to study the evolution of the required phase with respect to the variation in the calcinations temperature. Calcination is mainly conducted to remove the un-burnt volatile species and to avoide the shrinkage process during sintering [27]. The samples were calcined in the temperature range from 250 to 800^oC to determine the optimum calcination condition. The powder X-ray diffraction patterns of CdFe₂O₄ calcined at different temperatures are depicted in Figure 2. It was observed that formation of spinel CdFe₂O₄ structure, along with the other impurity phases, was observed in the samples calcined at, as prepared, 400° C and 800° C. The sample calcined at 600° C exhibited a sharp, intense diffraction peaks and single cubic phase with fcc structure of CdFe₂O₄ without any impurity phase [Ref. JCPDS card no.22-1063(79--1155) and Fd₃m (227) space group], revealing the highly crystalline character of the sample. The average crystallite size was determined by Debye-Scherrer's formula was found to be 17, 20, 22 and 40nm with respect to calcination temperature, as prepared, 400, 600 and 800° C respectively and the calculated lattice parameters α for CdFe₂O₄ sample was found to be 0.869 nm, which is in good agreement with the literature value of 0.869 nm for CdFe₂O₄ sample [28,29]. This indicated that impurity free CdFe₂O₄ nanoparticles were obtained at 600° C.

The scanning electron microscopy studies were undertaken for the sample calcined at 600° C. SEM photograph is shown in Figure. 3. A well-densified micro-structure can be observed from the photograph. It is evident from the SEM micrographs that CdFe₂O₄ sample have uniform and spherical structural morphology with a narrow size distribution of the particles. Figure. 4 illustrate the XEDS analysis of the CdFe₂O₄ sample calcined at 600° C, which shows that Fe, Cd and O atoms are the main components present in the sample. Figure 4. suggesting that the atomic ratio of Cd:Fe is (very close) 1:2 which confirms the formation of the CdFe₂O₄ nanoparticles.



Fig.2. XRD patterns for photocatalysts of CdFe₂O₄ calcined at different temperature for 2h.



Fig. 3 Scanning electron micrographs of cadmium ferrite sample calcined at 600°C

3.2. FTIR analysis

FTIR spectra were recorded in the range of 400–4000 cm⁻¹. Figure 5 shows the FTIR spectra of the CdFe₂O₄ samples calcined at different temperatures varying from 250 to 800°C. In the normal ferrites, there are two high frequency infra red lattice vibrations. These bands are v₁ andv₂ sensitive to changes in interaction between oxygen and cations in octahedral and tetrahedral positions and frequently appear in the ranges 600-540 and 450-400 cm⁻¹ respectively [30,31]. From figure 5, it has been observed that, with the increasing calcination temperature the disappearance of the absorption band at 1394 cm⁻¹ could be ascribed to the complete decomposition of the nitrate species and also, the intensity of O-H vibration of water molecules (1642 and 3438 cm⁻¹) decrease ie, complete elimination of water contents take place around 600° C and the crystallization of the spinel phase of CdFe₂O₄ [18, 19]. In our study v₁ band starts at 564cm⁻¹ and decreases to 531 cm⁻¹ as the particle size increases. Similar behaviour is observed for v₂ band which varies from 455 to 415 cm⁻¹ shown in table 1. This is a consequence of size effect. For nanoparticles, small changes in the environment of a chemical group will lead to small changes in the characteristic vibrational frequencies for this group. Here as the particle size decreases the increase in frequency (blue shift) and vice versa is observed [32-35].



Fig. 4 X-Ray energy-dispersive spectroscopy of CdFe₂O₄ sample calcined at 600⁰C.

Table.1

Calcination temperature (⁰ C)	Absorption Band	
	v ₁ (cm ⁻¹)	V ₂ (cm ⁻¹)
As Prepared	564	455
400	553	447
600	543	436
800	531	415



Fig. 5 FTIR analysis of the $CdFe_2O_4$ nanoparticles calcined at different temperature.

H. S. Bhojya Naik et al

3.3. Optical absorption spectra studies

The UV–vis absorption behavior of the prepared samples were analyzed due to their potential interest for photoirradiated applications. The optical characterization of cadmium ferrite samples were carried out by measuring the optical absorption spectra at room temperature. The UV–vis absorption spectra of the synthesized photocatalysts at different calcination temperature were compared and depicted in Figure 6. The result shows that the absorption band slightly shifted to the visible region with the increase in the calcination temperature upto 600° C. After that, sample doesn't show proper absorption in the visible region, this might be due to the nanostructure morphology, it doesn't retain its nanostructure morphology and displayed tremendous changes with respect to calcination temperature. The sample calcined at 600° C exhibits a good absorption for visible light due to desired crystalline nature. It is well known that, in the normal spinel-type compound CdFe₂O₄, tetrahedral and octahedral sites are occupied by Cd²⁺ and Fe³⁺ cations, respectively [36]. The band structure of CdFe₂O₄ is generally defined by taking the O-2p orbital as the valence band and Fe-3d orbital as the conduction band [37]. The absorption of CdFe₂O₄ in the visible light region may be due to the electron excitation from the O-2p level into the Fe-3d level. This makes it possible to utilize more percent of solar energy. So for cadmium ferrite samples, a better photocatalytic capability under solar light was expected [38].



Fig. 6 Optical absorption spectra of CdFe₂O₄ nanoparticles calcined at different temperature.

3.4. Optical studies

The optical energy bandgap (Eg) of the samples were calculated through the Tauc plots. The absorption coefficient α of the cadmium ferrite nanoparticles has been determined from the absorption data by using the fundamental relationships [39,40].

$I = I_0 e^{at}$	(3)
$A = \log(I_0/I)$	(4)
and	
$\alpha = 2.303(A/t)$	(5)

Where, A is the absorption and t is the thickness of the Cadmium ferrite samples. To estimate the optical absorption edge for these nanoparticles, $(\alpha h\nu)^{1/n}$ was plotted as a function of the photon energy hv for different n values (n=1/2, 3/2, 2, 3) (Tauc plots) [41]. The best linear fit was obtained in the case of n = 1/2, which indicates a direct allowed optical transition in cadmium ferrite nanoparticles. The Tauc plot is presented in Fig. 7. The straight line fit to the $(\alpha h\nu)^{1/n}$ vs. hv plot is obtained by using linear regression software with only very small standard deviation. The intercept of the line at $\alpha = 0$ gives the value of the optical absorption edge.



Fig. 7 Plot of $(\alpha h \nu)^2$ as a function of photon energy $h\nu$ (eV) for CdFe₂O₄ nanoparticles.

Figure. 7 shows the variation of optical band gap for cadmium ferrite samples calcined at different temperature. For the cadmium ferrite nanoparticles (as prepared, 400, 600 and 800^{0} C) the estimated band gap energy values were found to be approximately 1.74, 1.61, 1.47 and 0.65eV respectively. The sample calcined at 600^{0} C shows a band gap approximately 1.47eV, this result mach well with our previous report [28]. It must be noted that the bandgap energy of cadmium ferrite tends to decrease as the temperature is increased. This behaviour can be better understood if one considers that the interatomic spacing increases when the amplitude of the atomic vibrations increases due to the increased thermal energy. This effect is quantified by the linear expansion coefficient of a material. An increased interatomic spacing decreases the potential seen by the electrons in the material, which in turn reduces the size of the energy bandgap [42]. These energy absorption results open the possibility of using cadmium ferrite as a photoactive material in a broader electromagnetic spectrum range. These band gap energies are greater than the theoretical energy required for water splitting ($\lambda > 1.23$ eV) [43], thus, they are suitable for the role of solar light active photocatalysts.

3.5. Photocatalytic activities

To reveal the effect of calcination temperature on the photocatalytic properties of cadmium ferrite, photocatalytic degradation of methylene blue under sun light irradiation was examined (the amount of photocatalyst is the same in all experiments, 100 mg in 100 mL of solution). As can be clearly seen in figure 8, methylene blue in aqueous solution could be hardly degraded in the absence of photocatalyst under solar light illumination. Whereas, the methylene blue aqueous solution was degraded by the addition of cadmium ferrite catalysts. It can be seen that the photocatalytic activity of cadmium ferrite, calcined at 600°C exhibits the highest under solar light irradiation. The sample calcined at 800°C shows little photocatalytic activity under solar light irradiation. The photocatalytic degradation efficiency of MB increases gradually with an increase in the calcination temperature up to 600°C. However, as the temperature is above 600° C, the degradation efficiency decreases rapidly. The optimal calcination temperature can be described in the following manner. In principal the bulk counterparts of the photocatalysts show high photocatalytic activity, mainly due to their high cystallinity. In the present case, it is expected that the photocatalyst cystallinity should increase with increase in the calcination temperature. Consequently, all the samples showed improved cystallinity. As far as distinct difference is concerned, in the case of the 600° C calcined sample it retained its nanostructure morphology and the surface area, whereas the other samples displayed tremendous changes with respect to their nanostructure morphology, porosity and specific surface. Such changes in turn hampered the photocatalytic properties in the samples other than the sample calcined at $600^{\circ}C$ [44]. However, when the calcination temperature is higher than 600° C, the specific surface area of the catalyst decreased considerably [As the calcination temperature increase the crystallite size increases, it is still below 22 nm as the heat treatment temperature increases up to 600°C. However the grain size increase up to 40 nm when temperature reaches 800°C], retarding the adsorption of the MB [45], as a result it shows poor photocatalytic activity.

The energy band gap and photoabsorption performance of the catalyst might also play an important role in influencing the activity of the sample calcined at different temperatures. The higher photocatalytic efficiency of cadmium ferrite sample calcined at 600° C in comparison with other samples can be correlated to its ability to absorb a larger fraction of visible light, as demonstrated in figure 6. The sample calcined at 600° C is a semiconductor having a relatively narrow band gap 1.47 eV which shows the more ability to absorb the visible light in comparison with other wide band gap samples (as prepared, 400° C and 800° C, the band gap energy was found to be 1.74, 1.61, and 0.65eV respectively). The energy band gap 0.65eV correspond to the sample calcined at 800° C is less than the theoretical energy required for water splitting ($\lambda > 1.23 \text{ eV}$) [43], which is responsible for the poor photocatalytic catalytic cativity. Due to lower band gap of sample calcined at 600° C, the number of electrons reaching the conduction band from valance band increases, that is, the electron density in the conduction band is relatively high. Consequently, the number of holes in the valence band also increases. Both these electrons and holes interact with surface bound H₂O or OH⁻ to produce OH⁺ radicals. This favors the formation of more OH⁺ free radicals, which are main active species in the photocatalytic degradation process [28, 46-48]. These results revealed that cystallinity, calcination temperature, large visible light absorption and band gap energy factors make nanosized cadmium ferrite a more efficient photocatalyst under solar light irradiation.



Fig. 8 Degradation of methylene blue (10.0 mg L⁻¹) with different CdFe₂O₄ photocatalysts calcined at different temperature under solar light irradiation.

3.6 Recyclability of the catalyst

The recyclability of the cadmium ferrite samples were further investigated by performing recycling experiments. Figure 9. shows the performance of a recycled cadmium ferrite sample was measured under identical conditions over three recycle tests. There was no noticeable change in the photocatalytic activity of the recycled catalyst after three cycles under solar light irradiation, which indicated that the prepared cadmium ferrite sample displayed a high stability, recyclability and an efficient photoactivity during degradation of the organic pollutants under solar light irradiation.



Fig. 9 The photodegradation rate of MB in solution for 3 cycles using cadmium ferrite calcined at 600°C photocatalyst under solar light irradiation and the inset reveals the magnetic separation property of CdFe₂O₄-nanoparticle catalysts.

CONCLUSION

We have shown that, solar light active $CdFe_2O_4$ nanoparticles with narrow size distribution have been successfully prepared by a sol–gel auto-combustion reaction method. The absorption band of cadmium ferrite catalyst is wider, which displayed a continuous photoabsorption in the visible region; it makes use more percent of solar energy. The structural and optical properties of the nanoparticles point to a direct allowed transition in the nanoparticles. It should be pointed out that the cadmium ferrite calcined at $600^{\circ}C$ exhibited a high photocatalytic activity, excellent recyclability and durability properties and a good efficiency under solar light irradiation. In an attempt to design the solar light active photocatalyst, we were successful in optimizing the, calcination temperature, cystallinity, large visible light absorption and low energy band gap. The cadmium ferrite photocatalyst described here provides a new approach to the design of high-performance photocatalysts as green materials, ecofriendly photocatalyst and has tremendous potential application for practical use in the removal of organic pollutants and toxic water pollutants.

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