High Surface Area and Photo-catalysis of Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$
Nanocrystals in Degradation of Methylene Blue (MB)

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Abstract

Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ nanocrystals were obtained via co-precipitation strategy, and well-precisely scrutinized. XRD scrutiny affirmed the egress of the Nano-spinel phase for these nanocrystals existing in the Nano-regime. The teeny crystallite size R average value was 10.55 nm. All deduced parameters were affected by coexistence of Cu$^{2+}$, Cd$^{2+}$, Fe$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$ cations inside these nanocrystals. HRTEM images showed no accumulations for these Nano-spinels, where the average particle size value was 11.11 nm and was slightly bigger than the crystallite size R. Evaluation of photocatalytic activity for Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ Nano-spinel was acquired throughout the disintegration of Methylene Blue (MB) dye (1 × 10$^{-3}$ M and 2 × 10$^{-3}$ M) in aqueous medium under visible light (VL) irradiation using 100 Watt Tungsten lamp fixed at ~ 10 cm distance. As a result, usage of these new ultrafine Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ nanocrystals gives a new marvellous route for the advancement of cost-effective technologies for quite good waste H$_2$O recycling models, for raising H$_2$O quality and for the promotion of fruitful efforts in improving treatment systems.

Keywords:
Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ nanocrystals; HRTEM; Methylene Blue (MB); Photo-degradation; water treatment

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1. Introduction

Photo-catalysis progression for impure H2O treating is a serious target for environmentally ongoing inspection endeavors. Nano-spinels are soft-magnetic semiconducting nanocrystals possessing supreme persistence, and distinctly economical; thence these Nano-spinels are facilely fabricated and possess prevalent utilizations in marvellous prospects in NTC thermistors, electronical industries, magnetic refrigeration, ferrofluids and satellite communications [1-3]. Photo-catalytic efficacy for dye disintegration under visible light photons has exceedingly scrutinized within recent times. Organic dyes are vastly utilized in plentiful industries producing serious impact in nature causing adverse leverage on environmental prospects. Obviously, disintegration of such dyes is so serious, where disintegration via photo-catalysing is one of the most efficacious strategies for H2O up-cleaning [4]. Semiconducting photocatalytic strategy had targeted a marvellous route for environmentally polluted treating imputing to their entire disintegrations from organic contaminations into CO2 and H2O at ambient status [5]. Nano-spinels are utilized as one of prospective and gorgeous semiconducting nanocrystals; thence they have animated gorgeous scrutiny vistas imputing to their eminent features. Persistent endeavors have been protracted to persuade photocatalytic achievement of Nano-spinels [6]. Scrutiny endeavours in Nano-science have utility toward diverse prospects such: fabrication, exploration of newfangled nanostructures [7,8].

Distinctly, usage of Nano-spinel is so efficacious in disintegration of organic dyes, where these nanocrystals raise the efficacy of this procedure. This aspect has been early emphasized by [8], utilizing ZnFe2O4 in this aspect confirming their impress in dye disintegration. Thus, current scrutiny targeted the fabrication of new nanocrystals (Cu0.3Cd0.7CrFeO4 Nano-spinels) and distinguishing their merits. The second main target is getting water cleaned via simple strategy as inspecting their ability in MB disintegration. Evaluation of photocatalytic activity for Cu0.3Cd0.7CrFeO4 Nano-ferrites was obtained
through the disintegration of MB in aqueous medium under VL irradiation using 100 Watt Tungsten lamp fixed at ~ 10 cm distance.

2. Experimental Techniques

2.1. Preparation of Cu_{0.3}Cd_{0.7}CrFeO_{4} nanoparticles

As-prepared Cu_{0.3}Cd_{0.7}CrFeO_{4} Nano-spinels have been synthesized utilizing co-precipitation route according to the equation [9]:

\[ 0.3 \text{CuCl}_2.2\text{H}_2\text{O} + 0.7 \text{CdCl}_2 \cdot 2\text{H}_2\text{O} + \text{CrCl}_3.6\text{H}_2\text{O} + \text{FeCl}_3 + 8 \text{NaOH} \rightarrow \]
\[ \text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4 + 11.3 \text{H}_2\text{O} + 8\text{NaCl} \]

Co-precipitation methodology has been early reported [10]. Metal Chlorides are mixed together; then NaOH was added dropwise until PH=12; thence heated up to 80 °C/2h, thereafter precipitated, washed, dried, thence ground.

2.2. Characterizations:

Nano-ferrite powder was inspected via GNR APD 2000 Pro X-ray diffractometer step scan type and CuKα1 radiation at wavelength \( \lambda = 1.540598 \) Å [11]. FT-IR spectra was explored via Bruker-Tensor-27-FT-IR - type in the range from 200 to 2000 cm\(^{-1}\) [12,13]. Moreover, morphology was scrutinized via JEOL JEM – 2100 Electron Microscope. UV–vis spectra were registered using SPECTRO UV–VIS DUAL BEAM 8 AUTO CELL UVS-2700 scan-type spectrophotometer in the wavelengths 190 – 1200 nm at ambient temperature.

2.3. Photocatalytic activity of Cu_{0.3}Cd_{0.7}CrFeO_{4} nanocrystals:

Photocatalytic features of Cu_{0.3}Cd_{0.7}CrFeO_{4} nanocrystals were scrutinized via photo-disintegration of the simulated dye wastewater of MB solution under VL irradiation utilizing 100 Watt Tungsten lamp fixed at ~ 10 cm distance, as illustrated in Fig. 1. Aqueous suspension of MB-dye (1 × 10\(^{-3}\) M and 2 × 10\(^{-3}\) M) and Cu_{0.3}Cd_{0.7}CrFeO_{4} nanocrystals as photo-catalysts (0.1 g) were placed in a glass beaker. Prior to irradiation, each suspension was stirred in dark for 2 hrs to establish adsorption-desorption equilibrium (between photo-catalysts and dye), followed by VL irradiation utilizing 100 Watt Tungsten lamp fixed at ~ 10 cm distance. At time spans (20 min), 3 mL of suspension was taken from beaker, and then filtered to remove solid powders. Thence, solutions analysed by UV–VIS scan-type photometer in the wavelengths 190 – 1200 nm at ambient temperature to obtain relative
concentration variations of solution. Curve about concentration variations \( \frac{C}{C_0} \) as a function of time was plotted, where \( C \) presented concentration of MB at each time interval and \( C_0 \) was initial concentration of MB after reaching adsorption-desorption equilibrium [14].

3. Results and discussion

3.1. X-ray diffracting plots (XRD)

\( \text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4 \) nanocrystals affirmed egress of Nano-spinel monocular-phase which was illustrated by XRD diagrams in Fig. 2. Protruded peaks belong to Nano-spinel which was affirmed by matching with JCPDS card no. 00-001-1111. Plainly, for teeny Nano-size merit of these Nano-samples; so that emerges relatively wider XRD summits in Fig. 2, as affirmed regarding the teeny crystallite sizes as pointed in Table 1. Lattice cons a is ranging \( \approx 8.506 \text{ Å} \); agreeing with early scrutinized work [15]. Elucidated crystallite size R ranges \( \approx 10.55 \text{ nm} \), in Nano-scale ambit [16].

Obviously, S discloses reliance on both R and X-ray density \( D_s \), and \( \varepsilon \) relies on R. They possess big specified surface area S imputing to their teeny R [17]. S and \( \varepsilon \) values are illuminated in Table 1, matching well with early scrutiny [18]. Cell volume V and \( D_s \) are presented in Table 1.
3.2. Structural Phase Analysis

3-Dimensional cell volume was contrived utilizing the formulation [19]: \( V_{cell} = a^3 \).

3-Dimensional cell volume \( V \) disclosed a precise value reaching \( \approx 615.488 \) Å\(^3\), (Table 1).

X-ray density was contrived via the formulation [20]: \( D_x = \frac{ZM}{N_A V} \), Z is molecules no. per unit cell \((Z = 8)\); \( M \) is molecular weight and \( N_A \) is Avogadro’s no.

Dislocation density \( \delta \) was contrived via expression [21]: \( \delta = \frac{1}{R^2} \).

Distortion parameter \( g \) was contrived via formulation [18,21]: \( g = \frac{\beta_v}{\tan \theta} \).

Table 1 discloses dependence of \( g \) and \( \delta \) on \( R \) and \( \theta \), whilst \( g \) and \( \delta \) depend on oxygen ion concentration [21].

Specified surface area \( S \) of Nano-spinels contrived via formulation [17,18]:

\[
S = \frac{6000}{R_{XRD}D_x}
\]

Strain \( \epsilon \) of Nano-spinels was contrived utilizing the formula [17,18]:
\[ \beta \frac{1}{2} \cos \theta = \frac{0.94 \lambda}{R_{XRD}} + 4 \varepsilon \sin \theta \]

Strain \( \varepsilon \) interior these Nano-spinels affected by cations type and their crystalline configuration, (Table 1), as well as the protruded crystalline anisotropy [22]. Specified surface area \( S \) is \( \approx 97.74 \text{ m}^2/\text{g} \), assigning to teeny \( R \), (Table 1).

**Table 1** Lattice parameter \( a \), crystallite size \( R \), strain \( \varepsilon \), unit cell volume \( V \), X-ray density \( D_x \), specified surface area \( S \), distortion parameter \( g \) and dislocation density \( \delta \), error = ± 0.02.

<table>
<thead>
<tr>
<th>Nano-spinel</th>
<th>( a ) (Å)</th>
<th>( R ) (nm)</th>
<th>( \varepsilon )</th>
<th>( V ) (Å(^3))</th>
<th>( D_x ) (gm.cm(^{-3}))</th>
<th>( S ) (m(^2)/g)</th>
<th>( g )</th>
<th>( \delta ) (nm(^2)) × 10(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}<em>{0.3}\text{Cd}</em>{0.7}\text{CrFeO}_4 )</td>
<td>8.506</td>
<td>10.55</td>
<td>-0.098</td>
<td>615.488</td>
<td>5.818</td>
<td>97.74</td>
<td>0.0436</td>
<td>0.898</td>
</tr>
</tbody>
</table>

3.3. FT-IR Spectral plots

Infrared plot for \( \text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4 \) nanocrystals was registered from 200 to 2000 cm\(^{-1}\) in Fig. 3. Protruded vibrational summits illuminated in Table 2. 6-summits of \( \nu_1 \), \( \nu_2 \), \( \nu_4 \), \( \nu_A \), \( \nu_B \) and \( \nu_T \) egressed in FT-IR plots. \( \nu_i \) at 615.3 cm\(^{-1}\) and \( \nu_2 \) at 501.5 cm\(^{-1}\), (Table 2), referred to substantial sprawl oscillations of A-occupational allocations ligations; whereas enormous recapture strengths for bond-bending oscillations subsist on B-occupational allocations [23]. Predominately, affirmation of emersion of Nano-spinel configuration is affirmed by entity of both \( \nu_1 \) and \( \nu_2 \). Likewise, vibrational summit at 223.7 cm\(^{-1}\) for \( \nu_4 \) referring to lattice oscillations and it relies on the ligaments, \( \text{Fe}^{2+} - \text{O}^2^- \), \( \text{Cd}^{2+} - \text{O}^2^- \) and/or \( \text{Cu}^{2+} - \text{O}^2^- \) [10, 24]. Ternary summit \( \nu_T \) at \( \sim 1638 \text{ cm}^{-1} \) assigning to conserved \( \text{H}_2\text{O} \) in Nano-Crystals [25]. Summits around 910.4 and 1053 cm\(^{-1}\), are pointing to suprimes \( \nu_A \) and \( \nu_B \). \( \nu_A \) refer to coexistence of \( \text{Fe}^{2+}, \text{Cd}^{2+} \) amongst A- sites. \( \nu_B \) refer to coexistence of \( \text{Fe}^{4+}\text{O}^2^- \) and \( \text{Cr}^{3+}\text{O}^2^- \). Protrude of \( \text{Fe}^{4+} \) impute to electron jumping in-between \( \text{Fe}^{3+} \) and \( \text{Cr}^{3+} \) [10].
Debye temperature was deduced via the formulation [26]:

$$\theta_D = \frac{\hbar C v_{av}}{k} = 1.438 v_{av} \quad \text{and} \quad v_{AV} = \frac{v_1 + v_2}{2}$$

; $v_{av}$ is mean value of wave no's of oscillational suprises, $\hbar = h/2\pi$, $h$ is the Plank's cons, $k$ is Boltzmann's cons, $C = 3 \times 10^{10}$ cm/s; $C$ is light speed and $\hbar C / k = 1.438$ for Nano-spinels [26]: $\theta_D$ nearly $= 802.95$ K [27].

Concerning specified thermic theorem; the egress of conduction electrons portion (n-type transporters) procuring somewhat of thermic potency declining its saucepan, and this bolsters the connotation that conduction impute to electrons, and vice versa. Sill threshold frequency $\nu_{Th}$ is subsisting at 744.447 cm$^{-1}$ assigning to transition electrons, whilst $\nu_{Th}$ can be picked up via supreme spot of FT-IR plots [26,27]; thence, conduction electron no's possess impact on $\nu_{Th}$ and $\theta_D$. Force cons $F_1$ and $F_2$ equals $2.772 \times 10^5$ and $1.841 \times 10^5$ dyne/cm, assuring reliance of $F_1$ and $F_2$ on A- and B-sites oscillational frequencies, (Table 2).

Substantially, Threshold energy deduced via formulation [13]:

$$E_{Th} = \hbar C \nu_{Th}$$

Deduced evaluation of $\nu_{Th}$ and $E_{Th}$ are illuminated in Table 2.
Threshold supreme $\nu_{th}$ emanated around 744.447 cm$^{-1}$ conveying towards bigger frequencies assigning to high concentration of Fe$^{2+}$ and Fe$^{3+}$ and also assigning to hopping status as illuminated in the following expression:

$$\text{Fe}^{2+} + \text{Fe}^{4+} \leftrightarrow \text{Fe}^{3+}$$

The threshold energy $E_{th}$ possesses high evaluation as that of $\nu_{th}$, (Table 2).

Table 2 FT-IR vibrational summits positions $\nu_n$, $n = 1, 2, \ldots$ and B, Threshold frequency $\nu_{th}$.

<table>
<thead>
<tr>
<th>Nano-spinel</th>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>$\nu_2$ (cm$^{-1}$)</th>
<th>$\nu_4$ (cm$^{-1}$)</th>
<th>$\nu_A$ (cm$^{-1}$)</th>
<th>$\nu_B$ (cm$^{-1}$)</th>
<th>$\nu_T$ (cm$^{-1}$)</th>
<th>$\nu_{th}$ (cm$^{-1}$)</th>
<th>$E_{th}$ (eV)</th>
<th>$\Theta_D$ (K)</th>
<th>$F_1 * 10^5$ (dyne/cm)</th>
<th>$F_2 * 10^5$ (dyne/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{0.3}$Cd$</em>{0.7}$CrFeO$_4$</td>
<td>615.3</td>
<td>501.5</td>
<td>223.7</td>
<td>910.4</td>
<td>1053</td>
<td>1638</td>
<td>744.447</td>
<td>0.0925</td>
<td>802.95</td>
<td>2.772</td>
<td>1.841</td>
</tr>
</tbody>
</table>

3.4. HRTEM images

HRTEM pics of Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ Nano-spinels are illuminated in Fig. 4. These nanoparticles are not aggregated. Mean nanoparticle size $Z$ reaches $\approx 11.11$ nm. $Z$ evaluation is closer to that of R [15,28].
3.5. Photocatalytic features:

Photo-catalytic activities of teeny $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$ Nano-spinels for the sequent decolourization of Methylene Blue (MB) dye ($1 \times 10^{-3}$ M and $2 \times 10^{-3}$ M) in aqueous solution under VL irradiation via 100 Watt Tungsten lamp fixed at ~ 10 cm distance, examined under surging of sequent spans of time up to 180 minutes, (time duration is 20 min) were affirmed in Fig. 5 and Fig. 6. All of the catalytic disintegration reactions followed pseudo-first-order kinetics, evidenced by plotting of $(C/Co)$ against time (min), as well as plotting of $\ln (C/Co)$ against reaction time (min), (Fig. 5 and Fig. 6). It is explicit that, MB concentrations continuously decline with surge of stirring time emphasizing the photocatalytic activity of these Nano-spinels [29]. Disintegration Efficiency was elicited utilizing the following expression [30]:

![HRTEM pics of As-prepared Nano-spinel $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$.]
Degradation – Efficiency = \left( 1 - \frac{C}{C_0} \right) \times 100

Photo-catalytic efficiency of teeny Cu_{0.3}Cd_{0.7}CrFeO_{4} Nano-spinels for MB disintegration was explicitly explored on Fig. 5 and Fig. 6, proofing surging of their capability and activity in photo-degradation of MB dye, and referring to how high quality will be the treated H₂O by this procedure.

Manifestly, precise utilization of the extremely teeny Cu_{0.3}Cd_{0.7}CrFeO_{4} nanocrystals protrude a new exquisite route for the promotion of echo-friendly technologies for quite delicate waste H₂O reclaiming archetypes, for surging H₂O quality and for the furtherance of effectual exertions in ameliorating treatment mechanisms.
Fig. 5 Photo-catalytic efficiency and Photo-Degradation of MB $(1 \times 10^{-3} \text{ M})$ utilizing $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$ Nano-spinels as photo-catalysts, with time duration 20 min.
Fig. 6 Photo-catalytic efficiency and Photo-Degradation of MB ($2 \times 10^{-3}$ M) utilizing Cu$_{0.3}$Cd$_{0.7}$CrFeO$_4$ Nano-spinels as photo-catalysts, with time duration 20 min.

Fig. 7 sheds light on the sequent photocatalytic degradation mechanism of Methylene Blue (MB) dye ($1 \times 10^{-3}$ M and $2 \times 10^{-3}$ M) in aqueous solution under VL irradiation using 100 Watt Tungsten lamp fixed at ~ 10 cm distance, inspected under surging of sequent spans.
of time up to 180 minutes, (time duration is 20 min), utilizing \( \text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4 \) Nano-spinel that acts as photo-catalyst.

Fig. 7 The sequent photocatalytic degradation mechanism of Methylene Blue (MB) dye (1 \( \times \) 10^{-3} M and 2 \( \times \) 10^{-3} M), utilizing \( \text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4 \) Nano-spinel as photo-catalyst, under visible light irradiation, with time duration 20 min.

In Nano-ferrites the electrons from valency band are librated to conduction band leaving holes behind them in valency band with the aid of photons from 100 W Tungsten lamb. Electrons in conduction band unit with O2 and OH giving free radicals according to the following equations:

\[
e^- + O_2 \xrightarrow{\text{hv}} O_2^-
\]

\[
e^- + H_2O \xrightarrow{\text{hv}} H^+ + \cdot OH
\]
These free radicals attack MB dye with the help of photons from 100 W Tungsten lamb making degradation to the dye giving degraded products in the form of CO2 and H2O according to the following equation:

$$O_2^- + MB^{2+} \rightarrow \text{Degraded - Products}(H_2O + CO_2)$$

4. Conclusion

XRD inspection of the Ultra-teeny $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$ emphasized the egress of single-phase spinel configuration for these nanocrystals. Crystallite size R was $\sim 10.55$ nm. Elicited parameters were dependent on $\text{Cu}^{2+}$, $\text{Cd}^{2+}$, $\text{Cr}^{3+}$ and $\text{Fe}^{3+}$ cations in these Nano-spinels. HRTEM pics provided no accumulations for nanoparticles, where average particle size value was $11.11$ nm lightly rising than the crystallite size R. Photocatalytic activity for $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$ Nano-spinels was acquired through disintegration of Methylene Blue (MB) dye ($1 \times 10^{-3}$ M and $2 \times 10^{-3}$ M) in aqueous solution under VL irradiation using 100 Watt Tungsten lamp fixed at $\sim 10$ cm distance. Explicitly, utilization of $\text{Cu}_{0.3}\text{Cd}_{0.7}\text{CrFeO}_4$ nanocrystals confirmed obvious photo-disintegration for MB, with excellent efficiency.

Acknowledgments

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5. References


[5] T Li, Y Wang, Y He, J Cai, M Luo, L Zhao, Preparation and photocatalytic property of Sr$_{0.25}$Bi$_{0.75}$O$_{1.36}$ photocatalyst, Mater. Letters 74 (2012) 170–172. doi:10.1016/j.matlet.2012.01.078


[24] M Hashim, KS Alimuddin, SE Shirsath, RK Kotnala, H Chung, R Kumar, Structural properties and magnetic interactions in Ni$_{0.5}$Mg$_{0.5}$Fe$_{2-x}$Cr$_x$O$_4$ (0≤x≤1) ferrite nanoparticles, Powder Technology, 229 (2012) 37–44. doi:10.1016/j.powtec.2012.05.054


