Dual Functional Cobalt-doped CdFe2O4 nanoflakes for Promising Photocatalysts and Supercapacitor Electrodes

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ABSTRACT

Modern economic society is rapidly developing, leading to an increase in global energy demand due to the unnecessary burning of non-renewable fossil fuels, leading to energy crises and change in climate due to the inevitable production of organic dyes. Herein, the sol-gel auto-combustion method was used to fabricate cobalt-doped cadmium ferrite (Co-CdFe₂O₄) nanoflakes with cobalt 0.02%, 0.04%, 0.06%, 0.08% and 0.1% concentration. Prepared samples were characterized using XRD, SEM, UV-visible, and dielectric. XRD confirmed that pristine and Co-CdFe₂O₄ powder possessed spherical cubic crystal structure; no phase changes were observed after Co substitution. The dielectric constant, dielectric loss, and tangent loss were decreased at higher frequencies, and the effect of Co-doping was observed to change the dielectric properties significantly. After 35 minutes under visible light irradiation, the photocatalytic experiments presented exceptional photodegradation efficiencies against methylene orange (MO) (99.09%). The electrochemical results showed that the 0.1% Co- CdFe₂O₄ nanostructures offer an exceptional specific capacitance of 520.02 F/g, at of 1 mV/s scan rate. Such inexpensive and efficient photocatalytic electrode materials are required for energy storage applications and environmental protection.

Keywords: Co-doped CdFe₂O₄, Nanoflakes, visible-light-driven, Photocatalyst, supercapacitor

1. INTRODUCTION

The world's water and energy resources are under growing strain due to ongoing social and economic development and population [1, 2]. Globally, the development of industry and technology has resulted in many problems, including wastewater treatment and energy depletion. Wastewater contains extremely hazardous dyes that can affect wildlife, humans, and the environment [3, 4]. Environmental safety is threatened by the significant amount of toxic dyes in soils and water ponds, such as methyl orange (MO), methyl blue, and rhodamine B (RhB) [5]. Dyes are manufactured in almost 0.7 million tons annually, of which 12 percent are discharged directly during the dying procedure [6]. In addition to the pollution caused by the dye industry, the coloring material in sewer water can cause many harmful diseases, such as malignant

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neoplastic disease, DNA damage, pathology, and heart disease [7]. Various techniques were used to take down coloring material in wastewater, including adsorption, inverse osmosis, filtration, and photocatalysis [8]. The advantage of photocatalysis over adsorption is that photocatalysts oxidize dyes after they absorb solar energy with hydroxyl radicals. Therefore, photocatalysis can effectively degrade incredibly lasting, non-biodegradable dyes, pharmaceuticals, and chemical substances, which cannot be debauched by other conventional methods [9-12]. In addition, heterogeneous photocatalysis affects semiconductor nanostructures that take in photons from light and degrade pollutants through oxidization-reducing processes. Different photocatalysts have been fabricated to improve dye degradation efficiency over the last two decades [13-15].

Another threat is that International Energy Organization data indicates a massive annual electricity consumption of Terawatt hours (TWh) [16]. To solve the problem of energy depletion, researchers have developed new energy retention and transition systems, such as solar cells, fuel electric cells, batteries, and supercapacitors. Supercapacitor is considered a more efficient alternative to conventional capacitors and secondary batteries [17-19]. The fast charge and discharge behavior of supercapacitors and their high-power density make them an efficient alternative to secondary batteries. Supercapacitors are classified as an electrical dual-sheet capacitor (EDLC) and a pseudocapacitor (PC) according to their energy-retention mechanism, faradic and non-faradic, respectively [20, 21]. PCs tend to attract more attention than EDLCs because of their conspicuous specific capacitance. Better PC performance is caused by redox reactions occurring between electrodes and adsorbed electrolyte ions on the electrode surface. Therefore, many efforts have been made to develop cost-effective electrode material for PCs, as much as transition metallic-support-

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ed oxides, hydroxides, sulfides, selenides/tellurides, and conducting polymers [22, 23].

Ferrite-based pseudocapacitive materials have garnered more attention recently due to their superior chemical stability and metallic active sites in aqueous electrolytes. Several oxidation states make the material more redox stable, thus increasing its storage capacity. It has been widely accepted that compounds could be perfect electrodes for energy retention and transition due to their continuous current transmission, first-class pseudocapacitive place, reduced ion-diffusion distances, big capacitances for electrochemical reactions involving faradaic reactions, and resistance to mechanical impairment [24, 25]. Nanostructure can significantly enhance the performance of a supercapacitor since it contains many active sites, has a large specific surface, and has a short diffusion path [26-28]. Aside from ferrites, cadmium ferrite is preferable to other ferrites due to their soft magnetic properties, high chemical stability, and high electromagnetic performance, In these types of structures, cadmium ferrites have a reverse spinel construction where ferric ions (Fe³⁺) are evenly dispersed along some octahedral and tetrahedral lattice sites, but cobalt ions (Co²⁺) are distributed only in octahedral lattices, as a result of these different distributions, there are 56 ions in both the octahedral and tetrahedral structures [29, 30]. Cadmium ferrite is an average spinel with Cd²⁺ occupying tetrahedral sites and Fe³⁺ inhabiting octahedral pieces of land [37], by doping these ferrites with various divalent metal, such as Cd, Zn, Co, Ni, and Cr, their properties can be significantly altered [31-33]. The magnetic, optic, and electrical geographical area of these materials can be affected by changes in the distribution of divalent cations [34]. Doping of cadmium ferrites with other divalent metals can significantly increase their catalytic and electrode efficiency [35]. According to Tatarchuk et al. [36], as the quantity of doping with Co enhanced, the crystal magnitude enhanced from 37 nm to 51 nm, and the optic band gap reduced from 1.81 eV to 1.31 eV. Likewise, Cai-Yun et al. [37] reported that cobalt ferrites could be synthesized easily and were used to degrade organic dyes such as MB and RhB. They recovered that cobalt ferrites were first-class photocatalysts in the change of state of coloring material with chemical process rates of 0.198/min and 0.213/min, respectively. An Al-doped nano ferrite photocatalyst reported by Naseem et al. [38] degraded MB dye using 1 g of the catalyst with an efficiency of 93%. Zinc ferrite and Zinc ferrites doped with cobalt have also been studied for their degrading abilities and energy storage potentials. These types of materials can be synthesized in various ways to achieve the desired shape and structure. In addition to their cost-effectiveness, ability to produce atoms of the in-demand size and form, and chemical homogeneousness, co-precipitation, auto-combustion, sol-gel, hydrothermal, and solvothermal methods are the fewest popular natural science methods [39, 40]. The sol-gel combustion method is one of the fewest widely used natural science approaches to achieve desired properties[41].

In this work, the sol-gel auto-combustion approach is utilized to fabricate pure and cobalt-doped cadmium ferrite nanoflakes with varying cobalt concentrations (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%). An as-fabricated series of prepared materials were defined by XRD, SEM, and UV-visible spectroscopy to evaluate the prepared materials' properties. Powdered X-ray diffraction (P-XRD) patterns revealed the cubic crystal structure with phase purity. Di-electric loss, dielectric constant, and tangent loss decrease at high frequencies, and co-doping significantly affect dielectric properties. The specific capacity of 500 Fg-1 was calculated using cyclic voltammetry at 1 mVs-1 scan rate. Absorption spectra of Co-CdFe₂O₄ exhibited an edge in the seeable orbit, which is promising for photocatalytic application. Under visible illumination, 99.09% of MO (methyl orange) dye was degraded in 35 minutes. As a result of the experiments, we demonstrated that co-doping in cadmium ferrite can enhance their properties for various applications. The salient features of the study are stated as follows:

- •The sol-gel auto-combustion approach is utilized to fabricate pure and cobalt-doped cadmium ferrite nanoflakes with varying cobalt concentrations (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%).
- •The designed electrode (0.1% Co-doped $CdFe_2O_4$) possessed a 520.02 Fg-1 specific capacitance at 1 mV/s scan rate.
- •The optimized catalyst (0.1% Co-doped $CdFe_2O_4$) exhibited 99.09% degradation against MO in 35 minutes of irradiation.

Cobalt-doped CdFe₂O₄ nanoflakes exhibit excellent potential for wastewater treatment, effectively adsorbing and degrading contaminants. Additionally, their unique properties make them suitable for various biological applications, such as drug delivery [42] and antimicrobial use.

2. EXPERIMENTATION

2.1 Materials and Method

The ferric nitrate $[Fe(NO_3)_3]$, Cobalt nitrate $[Co(NO_3)_2.6H_2O]$, and Cadmium Nitrate $[Cd(NO_3)_2.H2O]$ 99% pure were brought from Sigma Aldrich and used as initial materials to synthesize the pristine $CdFe_2O_4$ and $Co-CdFe_2O_4$ nanopowder. The organic fuel urea $(CO(NH_2)_2$ and glycine $(C_2H_5NO_2)$ were purchased from chemical stores and used as precursors.

The Pure CdFe₂O₄, 0.02%Co-CdFe₂O₄, 0.04%Co-CdFe₂O₄, 0.06%Co-CdFe₂O₄, 0.08%Co-CdFe₂O₄, and 0.1%Co- CdFe₂O₄ were prepared by sol-gel auto combustion approach. The schematic representation of process samples by auto combustion approach is shown in Fig. 1. Initially, cobalt nitrate, cadmium nitrate, (CO(NH₂)₂, and glycine (C₂H₅NO₂) and ferric nitrate were dissolved in the distilled water to shape a homogeneous solution. Then, the reaction solution was put on a hot plate and continuously stirred at 300 °C. the gel was formed, and product grinding was obtained with the help of mortar and pestle, and a homogeneous fine powder was prepared. Later being sintered at 1000°C for 4 hours, the powder was ground into a fine powder, and finally, the Co-doped CdFe₂O₄ nanopowder was obtained, and the nanopowder was preserved for further characterization.

2.2 Diagnostic techniques

Several diagnostic approaches were used to assess the characteristics of the nanomaterials. The X-R (ray) diffraction was carried out on a Bruker D8-Discover X-ray diffractometer instrument with Cu-K radiation ($\lambda = 1.5406$ Å) within the 2 θ range of 20° to 55°. Using a MAIA3 Tescan instrument, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were performed on prepared samples. FT-IR spectrometer (Model: L1600235) was used to investigate the functional group. UV-Vis spectrophotometer (Model: C7200) was used to assess the optical characteristics of the sample.

2.3 Photocatalysis measurements

The photocatalytic performance of the as-ready catalyst was evaluated in the presence of visible light. In an aqueous mixture of MO and 30 mg catalyst in 100 ml of distilled water in a glass beaker [41]. The mixed mixture was continually stirred while remaining dark for 30 minutes to achieve equilibrium between the MO and the photocatalyst. The finding solution was then opened to visible light. The Visible light origin was a Xenon lamp (100 W) to measure absorption; the suspensions were collected at intervals of every five minutes. In order to limit interference and eliminate catalyst particles, the mixture was filtered and separated prior to evaluation. The initial concentration (Co) is defined as the optimal absorption of MO solution at 483 nm.



Fig. 1 Flow chart for the synthesis of Co-doped CdFe₂O₄.

2.4 Electrode Fabrication

The GAMRY Reference 3000 (42012) electrochemical workstation was used to assess the prepared materials' electrochemical studies. The operative electrode was designed by using 80 wt. % of active substantial together with 15 wt. % activated carbon and 5 wt. % Nafion. Ni foam was glued with the slurry and dried at 70°C for six hours. This setup used three electrodes: a reference electrode of Ag/AgCl, a counter electrode of platinum wire, and an electrolyte of 2M KOH solution. To examine the electrochemical properties of prepared materials, electrochemical impedance spectroscopy and cyclic voltammetry (CV) were evaluated in this study.

3. RESULTS AND DISCUSSION

This section explains the experimental outcomes and thorough discussion on the sol-gel auto-combustion approach to fabricate pure and cobalt-doped cadmium ferrite nanoflakes with varying cobalt concentrations (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%).

3.1 Structural Properties

Fig. 2 (a, b) illustrates the X-ray diffraction (XRD) configurations of as-prepared samples, including pure CdFe₂O₄, 0.02% Co-CdFe₂O₄, 0.04% Co-CdFe₂O₄, 0.06% Co-CdFe₂O₄, 0.08% Co-CdFe₂O₄, and 0.1% Co-CdFe₂O₄. Fig. 2 (a) shows the typical powder XRD pattern of Pure CdFe₂O₄ nanopowder. The XRD result shows the cubic unit cell planes with corresponding angles $(220)_{20=29.01}$, $(311)_{20=34.26}$, $(222)_{20=35.61}$, $(400)_{20=41.92}$, $(422)_{20=51.52}$, $(511)_{20=54.81}$, $(440)_{20=60.15}$, and $(531)_{20=66.75}$, respectively. The (311) plane indicates the presence of the spinel phase. Meanwhile, the (220) and (422) planes are sensitive to how cations are distributed on the tetrahedral sites. The (222) plane, on the other hand, is sensitive to cations on the octahedral sites. In both pristine and Co-CdFe2O4 nanopowder XRD patterns, all peaks correspond to

the cubic spinel lattice of $CdFe_2O_4$. By using the classical Scherrer relationship, the average crystallite size calculated from the excitonic peak (311) [43].



Fig. 2 X-ray diffraction patterns of (a) Pure $CdFe_2O_4$ (b) Pure $CdFe_2O_4$, 0.02% $CdFe_2O_4$, 0.04% $CdFe_2O_4$, 0.06% $CdFe_2O_4$, 0.08% $CdFe_2O_4$, and 0.1% $CdFe_2O_4$ nano powder.

$$D = \frac{\kappa\lambda}{\beta_G \cos\theta} \tag{1}$$

Crystallite size was calculated using the following formula: λ is the X-ray wavelength (1.5405 Å), β G is the FWHM, k is Scherrer's constant (0.94), and θ is the slant of diffraction. As the doping concentration rises, the CdFe₂O₄ sample's crystal size reduce [44].

3.2 Morphological Analysis

The morphology of prepared samples series of pristine Cd-Fe₂O₄, 0.04% Co-CdFe₂O₄, 0.08% Co-CdFe₂O₄, and 0.1% Co-Cd-Fe₂O₄ nanopowder, as shown in Fig. 3 (a-d). The SEM images show distinct changes in morphology due to doping. The micrograph shows that pure CdFe₂O4 nanopowder grows in large quantities and exhibits a spherical cube-shaped morphology. The cube normally demonstrates clustering due to lattice-based magnetic interaction. A microcube covered by smaller nanorods can be seen in Fig 3(a), which demonstrates the morphology of pure CdFe2O4. As shown in Fig.3 (b-d), when co-doped in CdFe2O4, the morphology slightly changed from the spherical cubic to flacks-like morphology. Further doping the 0.08% Co-CdFe2O4 nanopowder resulted in cubic morphology with spherical nanosphere, as shown in Fig. 3 (c). Micrographs of Co-CdFe2O4 showing flack-like morphology with spherical nanoparticles are shown in Fig. 3(d).





Fig. 3 SEM micrographs of (a) Pure $CdFe_2O_4$, (b) 0.04% Co-CdFe₂O₄, and (c) 0.08% Co-CdFe₂O₄, and 0.1% Co-CdFe₂O₄ at 1m scale.

3.3 UV–Visible Spectroscopy

To investigate the optical geographical area of prepared nanomaterials, UV-visible spectroscopy (PEAK instrument model: C 7200) was used to obtain absorption spectra [45]. This analysis exposed the synthesized materials to visible or ultraviolet light to promote electrons to higher energy states. The absorption spectra of Pure CdFe₂O₄ and CdFe₂O₄ doped with varying percentages (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%) of Co, as illustrated in Fig. 4 (a-b). Distilled water served as the solvent for these measurements. An excitonic absorption prominent peak at 464 nm was determined in the absorption spectrum of Pure CdFe₂O₄ (Fig. 4(a)); apart from the prominent peak in the graph, no other peak indicates a high optical response. Fig 4 (b) exhibited the absorption pattern of pristine CdFe₂O₄ and Co-CdFe₂O₄ with different cobalt concentrations (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%). CdFe₂O₄ showed a notable shift towards higher intensity peaks as Co dopants were added. Due to its high absorption intensity, the ferrite can be utilized as a visible-light-involuntary photo catalyst [46].





Fig. 4 (a) U.V visible spectroscopy of pure $CdFe_2O_4$ (b) Pure Cde_2O_4 , 0.02% $CdFe_2O_4$, 0.04% $CdFe_2O_4$, 0.06% $CdFe_2O_4$, 0.08% $CdFe_2O_4$, 0.1% $CdFe_2O_4$ nanopowder.

3.4 Dielectric properties analysis

The applied electric field usually causes dielectric relaxation by causing the electric dipole to move. Electric fields change dielectric material properties based on the Debye-Scherer relaxation model. The Debye-Scherer relaxation model is a simplified approach to understanding relaxation processes in dielectrics subjected to alternating electric fields, particularly concerning polarization and scattering. When an external electric field is applied, the dipoles in the material align with the field. Upon removal of the field, these dipoles return to random orientations, a process known as relaxation. The model posits that this relaxation follows an exponential decay pattern, characterized by a single relaxation time (τ) that indicates the rate at which dipoles regain equilibrium. It is most effective for systems where all dipoles experience similar environmental conditions [47]. The relation (Eq. 2) can be used to calculate the complex dielectric constant:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{2}$$

There are three types of permittivity: complex, imaginary, and accurate. The stored energy of materials in the presence of an applied field is described as follows (Eq. 3):

$$\varepsilon' = \frac{C_{\parallel}d}{A\varepsilon_o} \tag{3}$$

This formula is based on the parallel plate capacitance, the pellet area, and the pellet thickness. Fig. 5 (a) displays the dielectric constant's frequency dependency throughout a frequency orbit of 0 to 3 GHz. Co-CdFe₂O₄ exhibits a higher dielectric constant than pure CdFe₂O₄, which can be explained by the Maxwell-Wagner model [48]. The model is founded on the theory of Koop [49], which states that dielectric mediums consist of boundaries.

A higher frequency causes grain borders to be more active,

while a lower frequency causes grains to be more active. As a result of the strong polarization of the outer tract, charge carriers can move easily between grains and aggregates at grain borders. The polarization decreases with accelerative frequency and remains changeless at high frequency because the springing of electrons of different metal ions cannot track the fast AC field variations. As illustrated in Fig. 5 (b), energy was degraded in dielectric materials due to flaws and impurities in the crystal lattice. Fig. 5 (b). The polarizations lag behind the AC field when $tan\delta$ occurs. A major point to note is that tand approaches a constant value and drops significantly with frequency. The electrons follow the practical field and bounce between leads Cd2+ and Co3+ at lower frequencies. With higher frequencies, electrons lose high frequencies, so there is less hopping between Cd²⁺ and Co³⁺. With higher applied field frequencies, the tand is decreased. AC conductivity was determined using the formula.

$$\sigma_{\rm ac} = 2\pi f^{\mathcal{E}_0} \mathcal{E}' \tan \delta \tag{4}$$

Where "*f*" denotes the applied field's frequency.





Fig. 5 (a) Dielectric constant frequency dependence, (b) frequency dependency of dielectric loss, and (c) frequency dependency of AC conduction for (x = 0, 0.06, and 0.1%) Co-doped CdFe₂O₄ nano-powder.

In Fig. 5 (c), we show the variation of AC conductivity from 0 to 3 GHz at room temperature. Several conduction modes increase when frequency increases, including leaping, tunneling, and free band. Co increases AC throughout the entire frequency range when compared to pure $CdFe_2O_4$. When Co is added, the concentration of intrinsic donors increases, enhancing the hopping motion between Cd^{2+} and Co^{3+} and increasing the AC electrical conductivity.

3.5 Cyclic Voltammetry (CV)

By electrochemically measuring the redox process and charge transfer dynamics within a material under investigation with different examination rates (1, 5, 10, and 20 mV s-1), cyclic voltammetry was employed [50, 51]. Cyclic voltammetry (CV) Fig. 6 (a,b) shows CV curved shape for pure Cd- $\mathrm{Fe_2O_4}$ electrode and $\mathrm{CdFe_2O_4}$ doped with 0.1% Co electrode at various scan rates and their comparison at 1mVs-1. There are well-defined redox peaks observed in the designed electrode (pristine CdFe₂O₄ and Co-CdFe₂O₄); this indicates that the electrode is capable of storing charge through pseudocapacitive mechanisms [52]. The CV curve's area increased by accelerating the scan rate, suggesting improved reversibility and a higher charge storage capacity for the electrode. With the increase in scan rate, the CV curves' morphology is not affected as can be seen in Fig. 6 (a,b), suggesting the host material is more capable of mass transport and electron conduction [53]. Based on CV curves, the author calculated the Cp of the designed electrode materials [52]:

$$C_p = \frac{A}{2Km\nabla V} \tag{5}$$

In the equation, A represents the region enclosed by the curve, m represents the progressive mass, K represents the scan rate, and V represents the potential window. Cp values for Co-Cde₂O₄ electrodes were calculated at different sweep rates, and the maximum value was 520 F/g at 1 mVs-1, which is much higher than pure CdFe₂O₄.

3.6. Electrochemical impedance spectroscopy (EIS)

EIS techniques were utilized to characterize synthetic materials' electrochemical properties (current conductivity, internal resistance). EIS analysis was conducted at open circuit frequencies between 100 KHz and 0.1 Hz. In the low, medium, and high regions, supercapacitors often exhibit electrochemical characteristics halfway between those of capacitors and resistors. During low frequencies, the electrochemical system acts as a capacitor; during high frequencies, it acts as a resistance. The EIS pattern shows the semi-circle in the low to high-frequency range of the designed electrode of pure and Co-doped CdFe₂O₄, as exhibited in Fig. 7 (a, b). The 0.1%Co-CdFe2O4 sample has a much smaller semicircle diameter than Pure CdFe2O4. The smaller semicircle is characterized by low-level charge transportation opposition and high conductivity because of its increased conductivity. The vertical line is caused by ions diffusing between the electrolyte and electrode surface, indicating that the electrode material is close to an ideal capacitor [53]. Fig. 7 (c) compares the Nyquist plots of pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ samples. Calculated Charge Transfer Resistance (Rct) values for pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ are 0.07021 and 0.03302, respectively, as shown in Table 2. In bulk solutions, pure CdFe₂O₄ has a resistance of 1.773, and 0.1% of Co-CdFe₂O₄ has a resistance of 1.319, respectively. Hence, the Co-CdFe₂O₄ material with 0.1% Co exhibits good conductivity [54]. As demonstrated by the aligned formation in the lower frequency part, the electrode material shows fast ion diffusion, which indicates a perfect capacitive behavior.





Fig. 6 Cyclic Voltammetry (CV) of (a) Pure CdFe2O4 (b) 0.1% Co-CdFe₂O₄ (c) CV curves at 1 mV s-1 of Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ nanopowder.

Table 1Specific capacitance at various scan rates of Pure
 $CdFe_2O_4$ and 0.1% Co- $CdFe_2O_4$.

Electrode Ma-	20 mVs^{-1}	10 mVs^{-1}	5 mVs^{-1}	1 mVs^{-1}
Pure CdFe ₂ O ₄	42.31	53.21	60.02	88.07
0.1% Co- Cd- Fe ₂ O ₄	70.02	140.6	201.8	520.02

Table 2 EIS parameters of Pure $CdFe_2O_4$ and 0.1% Co- Cd-Fe₂O₄.

Material	Ru Ohm	Cdl F	Rct Ohm
Pure CdFe ₂ O ₄	1.773	0.00127	0.07021
0.1% Co- CdFe ₂ O ₄	1.319	0.00139	0.03302

3.7 Photocatalytic Degradation

To measure the degradation effect of synthesized material, the MO Dye was degraded by visible light (Xenon lamp 100 W) [55]. The intensity peaks were reduced observed in the MO dye's absorbance spectra every 5 min. Fig. 8 (a, b) shows how MO Dye gradually degrades with time, depicting progressive deterioration. In Fig. 7(a, b), Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ were used as catalysts for MO dye degradation in an aqueous medium. The MO degradation studies were performed under visible light irradiation. At first, Pure CdFe₂O₄ was used as a catalyst for their photocatalytic effect.

Catalytic batches were dispersed using 100 mL of MO solution (50 mg L-1) in a standard experiment. To balance adsorption and desorption, these reaction assemblies were placed in the dark for half an hour. The reaction assemblies were then allowed to equilibrate by being exposed to visible light. Accordingly, subsequent dye degradation studies of MO were done under visible light exposure because 0.1% Co-CdFe₂O₄ demonstrated faster degradation kinetics than Pure CdFe₂O₄ catalyst. To assess the decline in MO concentration, an absorption peak was seen at 483 nm [65].

A photocatalytic degradation based on surface phenomena, also called adsorptive photocatalysis, is required for the efficient degradation of MO. Experiments were conducted to study the photocatalytic degradation of MO under the same conditions. By monitoring the intensity of the peak at 483 nm, the author evaluated the progress of the photo-catalytic degradation of MO. Fig. 8 (c) display the graph for the defrent concentration ratios (C/ Co) of dyes over time (t), where Co shows the concentration of the MO before revelation, and C shows the absorption of the MO after t of radiation. To determine how fast a Dye degrades, pseudo-first-order kinetics can be used as shown in Fig. 8 (c, d) [56]. As shown in Fig. 8 (e), the superficial proportion constant (kapp) of the phot-catalyst was considered consuming the slope of the curve shaped between Co/C and time (t) corresponding to MO. Catalyst kapp and decolonization efficiency D (%) were calculated using the following formulas [67].

$$k_{app} = Ln \frac{C_0}{C} \tag{6}$$

$$D(\%) = \frac{Co - C}{C} \times 100 \tag{7}$$





Fig. 7 EIS spectra of (a) Pure CdFe₂O₄ (b) 0.1% Co-CdFe₂O₄
(c) EIS combined spectra of Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄, and (d) electrical equivalent circuit model.







Fig. 8 Time-dependent UV-vis spectra of photocatalytic decolonization of MO under visible light in the presence of (a) Pure CdFe₂O₄, (b) 0.1% Co-CdFe₂O₄, (c) plot of (Ct/Co) versus irradiation time of MO degradation by Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄, (d) plot of Ln(Co/Ct) versus irradiation time of MO decolonization by Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄, (e) Comparison of percentage and associated rate of constant for Pure CdFe₂O₄, 0.1% Co-CdFe₂O₄ photocatalyst, and (f) simple mechanism of MO dye degradation in presence of light and photocatalyst.

When the decomposition by light performance was tested with the developed catalyst present, as shown in Fig. 8. (e), it was discovered that the degradation for 0.1% Co-CdFe₂O₄ was significantly more than that of other fabricated catalysts. According to a pseudo-first-order kinetics-based dye degradation model, the produced catalysts exhibit a fine linear connection with dye decolonization. About 93.33% (± 0.0006578) and 99.09% (± 0.00933) of MO were degenerated by Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ in 35 minutes, respectively, when exposed to visible light (Fig. 8) (e) shows that Pure CdFe₂O₄ and 0.1% Co-CdFe₂O₄ degraded about 93.33% and 99.09% of MO during the course of 35 minutes, with linked constant rates (k) of 0.0976 min-1 and 0.1683 min-1, respectively. After 35 minutes of exposure to 0.1% Co-CdFe₂O₄, MO exhibits nearly total deterioration. The obtained data indicates that, in comparison to CdFe₂O₄ against MO assessed in this work, 0.1% Co-CdFe₂O₄ exhibits enhanced photocatalytic achieving. The catalyst that worked best, according to the results, was 0.1 Co-CdFe₂O₄.

The reaction mechanism of the photodegradation process is presented as follows:

$$CO: CdFe_2O_4 + hv \rightarrow CO: CdFe_2O_4 + (\boldsymbol{e}_{CB}^- + h^+)$$
(7)

$$CO: CdFe_2O_4 + (\mathbf{e}_{CB}) + o_2 + o_2^-$$
(8)

$$H_2 O \to H^+ + HO^- \tag{9}$$

$$H0^- + h^+ \to 0H^{\bullet} \tag{10}$$

$$0_2^- + H^+ \to HOO^{\bullet} \tag{11}$$

$$H00^{\bullet} + e^{-} \to H00^{-} \tag{12}$$

$$HOO^- + H^+ \rightarrow H_2O_2 \tag{13}$$

$$H_2O_2 + e^- \to HO^{\bullet} + HO^- \tag{14}$$

$$CO: CdFe_2O_4(H^+{}_{VB}) + H_2O \rightarrow HO^{\bullet} + H^+$$
(15)

$$Dye + HO^{\bullet} + \quad {}^{\bullet}O_2^- + CO_2 + H_2O \text{ (Intermediate)} \quad (16)$$

$$CO: CdFe_2O_4(h^+_{VB}) \to (\text{Oxidation}) \tag{17}$$

$$CO: CdFe_2O_4 + (\mathbf{e}_{CB}) \to (\text{Reduction})$$
(18)

A description of the mechanisms involved in MO dye decolonization is presented in Fig 8 (f), which is accompanied by the mechanism that occurs in the presence of light and photocatalyst. Accordingly, photo-excitation occurs when light illuminates because electrons and ions (h⁺) are formed in the conduction and valance band respectively, as shown in (Eq. 7). A photo-excitation phenomenon produces holes in the valence band. Electrons in the valence band are excited by gaining photons and moving to the conduction band during photo-excitation. The valence band leave vacancies, or "holes," as a result of this migration. Together with the excited electrons in the conduction band, these holes function as positive charge carriers, forming electron-hole pairs. Several activities, including charge separation in photocatalysis, where the holes can take part in oxidation reactions and increase the material's total photocatalytic activity, depend on these pairings. These holes oxidize as they react with hydroxyl (OH) ions or water surfaces to produce hydroxyl radicals. According to Eq. (8), electrons from the conduction band react with oxygen molecules on the surface of the photocatalyst to produce superoxide radicals. Superoxide radicals are used to prevent the re-combining of e⁻/h⁺ pairs. Moreover, the hydroxyl radical is formed due to the oxidation process in prepared photocatalysts in [Eq. (9-18)], which are

required for maintaining electron neutrality. After that, the generated hydroxyl radicals react with the MO dye to generate CO_2 , H_2O , and degraded products.

4. SUMMARY

In summary, Cobalt-doped cadmium ferrite (Co-CdFe₂O₄) Nano flakes with varying Co concentrations (0.02%, 0.04%, 0.06%, 0.08%, and 0.1%) were fabricated using facile Sol-gel auto combustion technique. Powdered X-ray diffraction (P-XRD) patterns revealed a cubic crystal structure in all samples. The dielectric loss, dielectric constant, and tangent loss were reduced at high frequencies after incorporating Co (dopant). As dopant content (Co) is increased, the energy band gap decreases, which can be attributed to variations in crystallite size and substitutions of the dopant ions. At 1 mV/s, the optimized sample (0.1% Co-CdFe₂O₄) showed 520.02 Fg-1 specific capacitance. The band gap energy was significantly affected by the Co content in Co-CdFe₂O₄, which is encouraging for photo-catalytic applications. Under visible irradiation, 99.09% of MO (methyl orange) dye was degraded within 35 minutes. Results showed that co-doping could enhance cadmium ferrite nanostructures' properties for various applications.

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