# Review Article: Semiconductor $ZnFe_2O_4$ as Efficient Photocatalyst for the Degradation of Organic Dyes: An Update

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## ABSTRACT

Zinc ferrite ($ZnFe_2O_4$) is one of the famous and widely studied photocatalysts with band-gap in the visible region. ZnFe2O4 has emerged as a promising photocatalyst due to its unique properties and versatile applications. This review aims to provide an overview of the properties, synthesis methods, and photocatalytic performance of zinc ferrite. It also explores the diverse applications of zinc ferrite composites as catalysts, highlighting their performance as photocatalysts. The catalyst possesses a spinal fine crystalline structure and can be prepared by various methods such as combustion, hydrothermal, sol-gel, and co-precipitation. Zinc ferrite by nature is a superparamagnetic semiconductor that has been used for the degradation of numerous organic dyes in the past. $ZnFe_2O_4$ is particularly effective in harnessing light energy and actively supports photocatalytic-redox reactions.

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## Content



## 1. Introduction

Dyes pollution is now a serious concern for living organisms all over the world. Organic dyes are poisonous, malignant, genotoxic, and have complex structures which are very perilous to aquatic and human health [1-3]. To solve the issue of water pollution resulting from the contamination of dyes, various treatment approaches have been implemented to effectively eliminate dyes from water. Among the prominent methods employed are advance oxidation [4], coagulation [5], adsorption [6, 7], membrane technology [8], and some biological methods [9]. Photocatalysis is a widely used technique for the degradation of these deleterious dyes in water and its importance is increasing day by day due to its ideal results. It is one of the most feasible processes because it requires an affordable and simple setup as compared to other complex treatment methods. In addition, this technique does not allow the formation of hazardous products and is less time-consuming and cost-effective [10-14].

Water pollution is proportionate to the increase in population because it gives rise to industrialization and urbanization. The release of dyes into rivers or water streams blocks the path of sun rays and decreases the COD and BOD value of water which results in the elimination of water ecology [15-17]. Everyday a very large amount of organic dyes are released from various industries into pure water bodies which are changing the physical and chemical nature of pure water and are resulting in highly venomous materials. Pure water will become scarce one day if the dye pollution is not controlled especially in developing countries because more than 25% of the water pollution is due to the discharge of dyes from various sources. Dyes possess very complex structures that render them non-biodegradable; thereby leading to their persistence in water for a long duration can potentially give rise to various waterborne diseases. Thus removal of such hazardous dyes is necessary to save various aquatic life as well as human health [17-22]

Photocatalysts are very useful for wastewater treatment and can be reused several times without any decrease in their efficiency [23-24]. $ZnFe_2O_4$ is one of the most investigated and important photocatalysts. Greater surface area, high activity, reusability, stability, biocompatibility, and electrical and magnetic resistance make $ZnFe_2O_4$ more useful as a photocatalyst. Generally, ferrites are formed in hexagonal, Garnet, and spinal depending upon their molecular formula [25-27]. This review explores the potential of zinc ferrite as a promising photocatalyst for various applications. With its unique properties and abundant availability, zinc ferrite has garnered significant attention in the field of catalysis. This review aims to analyze its efficiency,

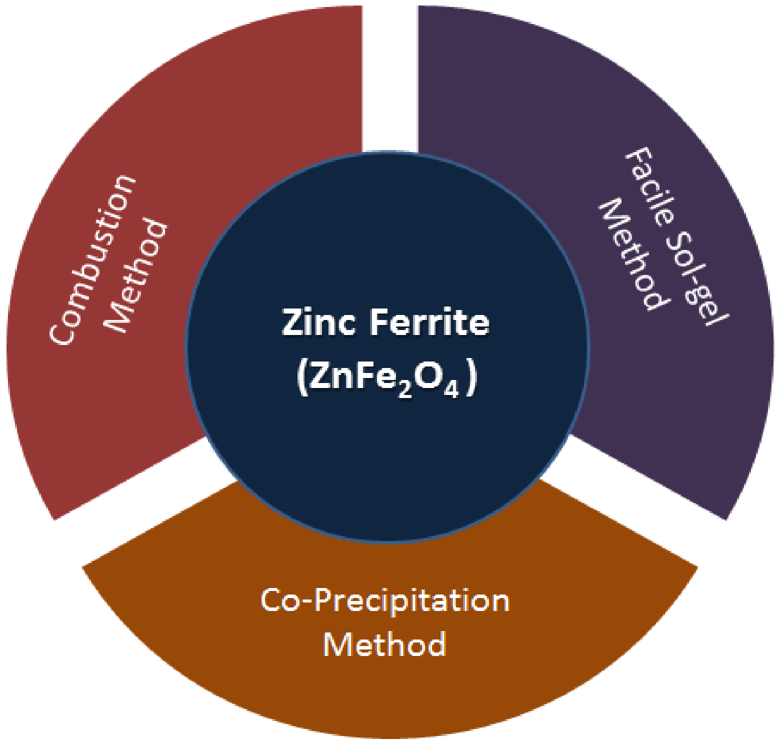


**Figure 1.** Common methods for the preparation of $ZnFe_2O_4$

stability, and versatility in harnessing solar energy for environmentally friendly processes.

## 2. Synthesis of ZnFe2O4 using Various Techniques

Zinc Ferrite nanoparticles can be synthesized using various methods such as co-precipitation, hydrothermal, sol-gel, combustion, and biosynthesis [26, 28]. The three most common and easy methods used for zinc ferrite synthesis are combustion, facile sol-gel method, and co-precipitation method (**Figure 1**) are given as follow.

### *2.1. Combustion method*

By combustion method, the nanoparticles of zinc ferrite were prepared using $Fe(NO_3)_3{\cdot}9H_2O$ (Iron nitrate nona-hydrated), $Zn(NO_3)_2{\cdot}6H_2O$ (Zinc nitrate hexa-hydrated), $CH_4N_2O$ (Urea) (99% purified), and distilled water. In this method, an aqueous containing 1:2 of $Fe(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ as well as a specific amount of $CH_4N_2O$ (99% purified) was prepared in 40 mL distilled water. The solution was heated at 70-80 °C with continuous stirring for about 30 min. After that, the solution was transferred into a muffle furnace and heated at 400-410 °C for 10 min. The obtained solid product was dried, crushed, and calcinated at 500-550 °C [29-30].

### *2.2.Facile sol-gel method*

By facile sol-gel method zinc ferrite nanoparticles was synthesized using $Fe(NO_3)_3{\cdot}9H_2O$ (Iron nitrate nona-hydrated), $Zn(NO_3)_2{\cdot}6H_2O$ (Zinc nitrate hexa-hydrated), $C_6H_8O_7$ (Citric cid), and $NH_3OH$ (ammonium hydroxide). In this method, a standard aqueous solution containing $Fe(NO_3)_3{\cdot}9H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$ (2:1, Fe and Zn) and $C_6H_8O_7$ was prepared. The prepared solution was heated at 70-75 °C for about 3 hrs. pH 7 was adjusted using $NH_3OH$ (known purity, 27-28% W/V), and the solution was again heated at 80 °C. The precipitate formed was dried, crushed, and was calcinated at 700-1000 °C [31].

### *2.3.Co-precipitation method*

In this method, $ZnCl_2$ (Zinc chloride), $FeCl_3$ (Ferric chloride), and NaOH (Sodium hyroxide) of analytical grade were used for the preparation of zinc ferrite nanoparticles. $ZncCl_2$ and $FeCl_3$ in 1:2 were dissolved in water. pH 7 was adjusted using NaOH (1 M) and the solution was heated at 60 °C for about an hour until complete dissolution of the reagents. The formed precipitate was washed with distilled water and organic solvent (Ethanol or acetone) and was centrifuged for further purification. The solid mixture obtained was dried, grinded, and calcinated at 800-1000 °C [32].

## 3. Photocatalytic Property

From the previous studies of zinc ferrite as a photocatalyst, it can be concluded that zinc ferrite is an effective photocatalyst that can work best in both visible as well as also in the UV region. The catalyst can degrade cationic [29], anionic [33], and neutral dyes [34], as listed in **Table 1**. The photocatalytic study using Zinc Ferrite has shown that the catalyst does not generate any harmful by-product and acts as a green catalyst. Zinc ferrite is a significant photocatalyst due to its paramagnetic nature, adsorption capacity, low band gap, photocatalytic reaction, stability, reusability, and sensitivity toward visible light [35]. From previous research in the past about zinc ferrite as a photocatalyst, it can be concluded that the catalyst mostly degrades the dyes in a time range of 30-120 min depending on the nature of the dyes. The catalyst has a band gap ranging from 1.8 EV to 2.5 EV depending upon its preparation method. The photocatalytic-redox reactions start when a photon interacts with $ZnFe_2O_4$ which results in the excitation of electrons from its valence band to the conduction band, this results in electron-hole pair production which supports the generation of $-O_2^{\bullet}$, $OH^{\bullet}$ free radicals. Enhancer ($H_2O_2$) is used in the photocatalytic study to further increase the production of OH• free radicals and to reduce the time for degradation. The radicals are produced to attack the targeted dye and convert it into nontoxic products [36-38]. **Figure 2** displays the general degradation mechanism of dyes using zinc. ferrite.

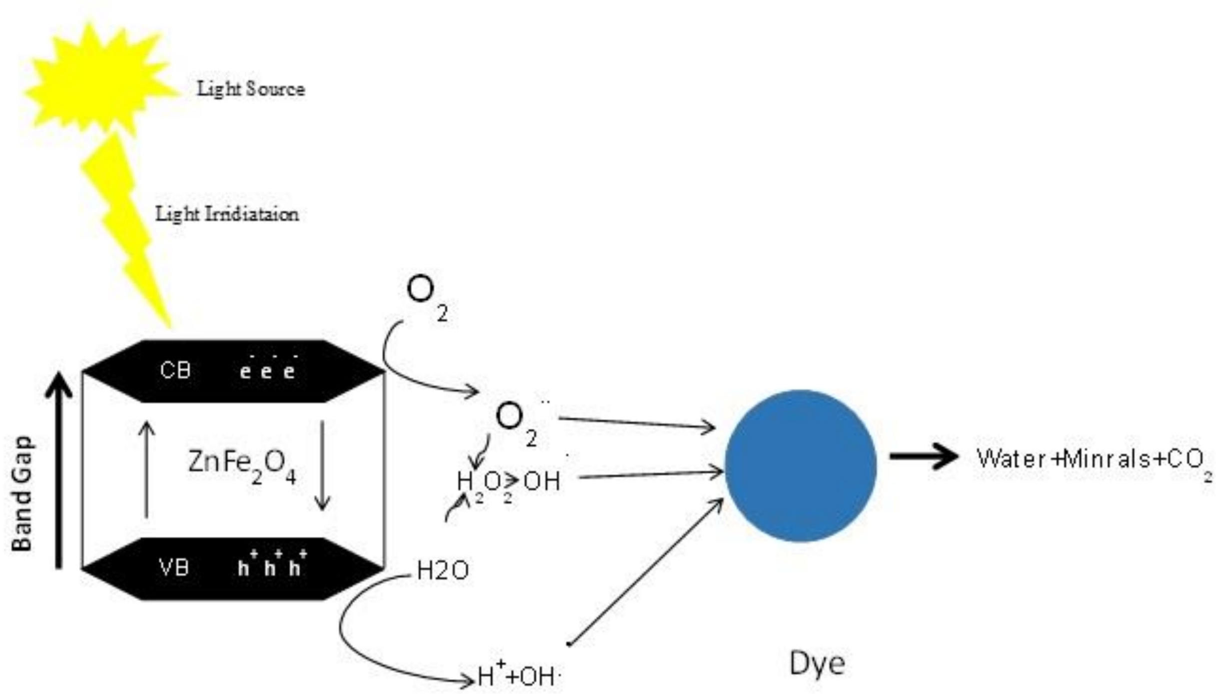


**Figure 2.** Mechanism of degradation of dyes using $ZnFe_2O_4$

**Table 1.** Degradation of various dyes using $ZnFe_2O_4$

| Method of catalyst synthesis | Dye | Dye Nature | Time (Min) | Degradation % | References |
|---|---|---|---|---|---|
| Combustion | Remazol Brilliant voilet-5R | Cationic | 30 | 99.9 | [29] |
| Co-precipitation | Crystal violet | Cationic | 30 | 96 | [39] |
| Co-precipitation | Diclofenac sodium | Anionic | 120 | 61.4 | [33] |
| Hydrothermal method | Carbamazepine | Neutral | 60 | 100 | [34] |
| Combustion | Rhodamine B | Cationic | 30 | 95 | [40] |
| Co-precipitation | Methylene blue | Cationic | 200 | 85 | [41] |
| Sol-gel method | Amido Black 10b | Cationic | 90 | 92 | [42] |
| Biosynthesis | Methylene blue | Cationic | 120 | 98 | [43] |

The general reactions involved in the degradation of dyes using $ZnFe_2O_4$ are:

$$ZnFe_2O_4 \xrightarrow[h^+_{(VB)}]{h\upsilon} ZnFe_2O_4^* (h^+ + e^-) \quad (1)$$

$$H_2O \longrightarrow H^+ + OH \quad (2)$$

$$O_2 + e^-_{(CB)} \longrightarrow {}^\bullet O_2^- \quad (3)$$

$$H_2O_2 + e^-_{(CB)} \longrightarrow HO^\bullet + OH^- \quad (4)$$

$$H_2O_2 \longrightarrow HO_2^\bullet + H_2O \quad (5)$$

$$Dye \xrightarrow{OH^\bullet / h^+_{(VB)} / {}^\bullet O_2^- / HO_2^\bullet} \text{Degradation product} \quad (6)$$

## 4. Zinc Ferrite Coupling with Other Compounds/Metals

Zinc ferrite has gained significant attention as a catalyst in composite form. The photocatalytic efficiency of $ZnFe_2O_4$ can be further enhanced by combining it with other materials, such as carbon-based supports (graphene, carbon nanotubes, etc.) or metal nanoparticles (Co, Al,Pd, Pt, Au, *etc.*) [44]. The efficiency of the composites depends upon the crystallinity, adsorption capacity, size of composite nanoparticles, method of preparation, and magnetic properties [36]. The study reported by [45] has shown that coupling with other compounds not only increases its efficiency of $ZnFe_2O_4$ rather it also decreases the time for the degradation of the selected dye. As a composite with metals and metal oxide, zinc ferrite exhibits excellent catalytic activity, stability, leaching resistance, and magnetic properties making it a promising photocatalyst [46–49]. **Figure 3** illustrates the general structure of the zinc ferrite composite and the charge transfer between the two semiconductors in the composite.

Zinc ferrite based composites have been employed in the catalytic degradation of organic pollutants, such as dyes and pharmaceutical compounds, due to their strong adsorption capability and efficient oxidative properties [50-52]. These composites offer several advantages, including increased surface area, and improved dispersion of the active phase. **Table 2** presents the photocatalytic performance of various zinc ferrite composites.

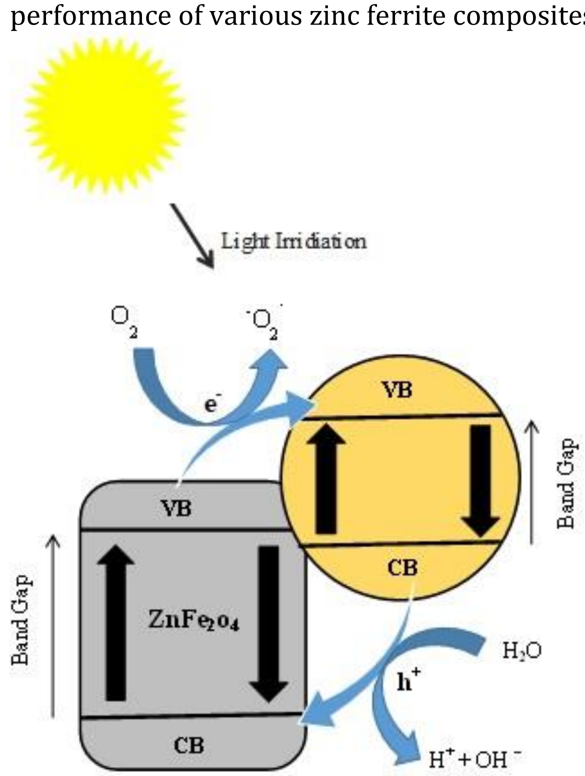


**Figure 3.** General sketch of charge transfer between semiconductors in $ZnFe_2O_4$ composites

**Table 2.** Degradation of dyes using $ZnFe_2O_4$ composites

| Composite | Preparation method | Dye | Dye nature | % Degradation | Time for degradation (Min) | Reference |
|---|---|---|---|---|---|---|
| Cobalt-zinc ferrite Co-$ZnFe_2O_4$ | Citrate precursor | Methylene blue | Cationic | 77 | 60 | [44] |
| Graphene oxide-zinc ferrite (GO/ $ZnFe_2O_4$) | Co-precipitation | Malachite green | Cationic | 100 | 60 | [45] |
| Graphene oxide-zinc ferrite (GO/ $ZnFe_2O_4$) | Co-precipitation | Fast green | Anionic | 100 | 60 | [45] |
| Graphene oxide-zinc ferrite (GO/ $ZnFe_2O_4$) | Co-precipitation | Eriochrome black T | Anionic | 100 | 60 | [45] |
| Cool fly Ash- Zinc Ferrite (CFA/ $ZnFe_2O_4$) | Hydrothermal | Methylene blue | Cationic | 97 | 60 | [47] |
| Zinc oxide-Zinc Ferrite (ZnO/ $ZnFe_2O_4$) | Hydrothermal | Malachite green | Cationic, Anionic | 99 | 70 | [46] |
| Zinc oxide-Zinc Ferrite (ZnO/ $ZnFe_2O_4$) | Hydrothermal | Methyl orange | Anionic | 98 | 120 | [25] |
| ZST ($ZnFe_2O_4/SiO/TiO_2$) | Sol-gel | Methylene blue | Cationic | 95 | 120 | [53] |
| Zinc ferrite/ silver/ silver chloride ($ZnFe_2O_4$/Ag/Agcl) | Co-precipitation | Methylene blue | Cationic | 98 | 90 | [54] |
| Dysprosium (Dy) doped zinc ferrite (Dy/ $ZnFe_2O_4$) | Co-precipitation | Methylene blue | Cationic | 99.8 | 60 | [55] |

## 5. Chemical and Physical Properties

Zinc ferrite nanoparticles have cubic spinal structures with $Zn^{2+}$ tetrahedral and $Fe^{3+}$ octahedral sites [56-57].They are paramagnetic and crystalline in nature [58] and have greater structural, mechanical, and thermal stability [26,59]. The nanoparticles of zinc ferrite are mostly spherical in morphology [29] and are inert to water [60-61] . The density of $ZnFe_2O_4$ is 5.34 g/cm$^3$ and has a relatively high melting point around 1450 °C [32]. Zinc ferrite possesses a greater surface area and has higher adsorption capacity which makes it a good photocatalyst [62, 63].

## 6. Conclusion

Zinc ferrite is a visible light active photocatalyst that can degrade cationic, anionic, and neutral dyes and shows its best efficiency for all. The catalyst possesses a greater adsorption capacity and can be reused several times. The catalyst is widely discussed in the past and has been reported as one of the most valuable and green catalysts due to its nature and properties. The catalyst generates free radicals in the solution which attack the dyes and degrade them. The generation of these free radicals can be increased further by adding a specific amount of $H_2O_2$ into the solution. The nanoparticle size and band gap of the catalyst may vary depending upon its preparation method. $ZnFe_2O_4$ shows better degradation efficiency for cationic and neutral dyes as compared to anionic dyes as a whole.

## Recommendation

Based on facts and figures reported in past research studies zinc ferrite is highly recommended as a photocatalyst to be used for the photocatalytic degradation of organic dyes. The technique is a low-cost feasible one; therefore, it is highly recommended to be adopted at large scale.

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