e-ISSN: 2582-5208
International Research Journal of Modernization in Engineering Technology and Science
(Peer-Reviewed, Open Access, Fully Refereed International Journal)
Volume:05/Issue:10/October-2023 Impact Factor- 7.868 www.irjmets.com

SYNTHESIS AND CHARACTERIZATION OF Cr/$ZnFe_2O_4$ NANOPARTICLES FOR HIGH PHOTOCATALYTIC ACTIVITY UNDER VISIBLE LIGHT

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ABSTRACT

Recently, researchers have focused a lot of attention on semiconductor photocatalysts, particularly heterostructures made of $ZnFe_2O_4$. In the disciplines of photocatalysis and energy storage, ZnO is a material that has received a lot of investigation due to its accessibility, toughness, and biocompatibility. It benefits the environment as well. Its actual utility is, however, constrained by the broad bandgap energy and fast recombination of the photoinduced electron-hole pairs of ZnO. Numerous methods, including the doping of metal ions and the development of binary or ternary composites, have been employed to overcome these problems. Recent research shown that when exposed to visible light, $ZnFe_2O_4$ heterostructures outperformed bare $ZnFe_2O_4$ nanostructures in terms of photocatalytic activity. This review mainly focused on the synthesis of $ZnFe_2O_4$ heterostructures and potential uses for them, such as the degradation of organic contaminants and the assessment of hydrogen. The significance of synthesis methods like controlled morphology and bandgap engineering was emphasized. Additionally, the Possible applications of $ZnFe_2O_4$ heterostructures in the field of photocatalysis. The mechanisms of photodegradation were studied. Lastly, problems with ZnOFe2O4 heterostructure Future possibilities have been addressed.

Keywords: Photocatalysis, Nanoparticles, Hydrothermal Process, X-Ray Diffraction, X-Ray Spectroscopy, Visible Light.).

I. INTRODUCTION

In the modern world, water contamination is a significant issue. It is brought on by several things, including sewage, agricultural runoff, and industrial pollution. Due to the quantity of organic and dye pollutants they produce, the textile industry is a significant contributor to water pollution. Both the environment and human health are negatively impacted by these contaminants. Here some of the health problems, including diarrhea, cholera, typhoid, dysentery, and other diseases and the environmental impacts are Loss of biodiversity, Economic impacts, Degradation of water quality, and Damage to ecosystems [1]. Photocatalysis is a potential technology for the treatment of water pollution. Materials called photocatalysts can degrade pollutants when they are exposed to sunshine. Organic pollutants can be particularly effectively broken down by semiconductor photocatalysts like ZnO and TiO_2 [6,9]. For the remediation of water pollution, photocatalysis is a promising method since it is economical, effective, and scalable. Various contaminants, such as organics, dyes, and heavy metals, can be treated with it. Photocatalysis has a wide range of applications, including Energy production, chemical-synthesis, disinfection, water treatment, air purification, self-cleaning surfaces, antibacterial surfaces, hydrogen production etc [11]. In the process of photocatalysis, a catalyst—typically a semiconductor—uses light energy to convert contaminants into safe compounds. As light energy is absorbed by the catalyst, electron-hole pairs are formed. The contaminants are subsequently reacted with by these electron-hole pairs, which transform them into safe chemicals [13].

II. LITERATURE REVIEW

Solvothermal method: irshad Ahmad et.al discovered that when ZnO is doped with aluminum and exposed to simulated sunlight, the degradation efficiency jumps to 98%. When aluminium is doped into ZnO, the band gap narrows from 3.67 eV to 2.96 eV. Aluminium is a donor impurity, which contribute electrons to the conduction band, thereby closing the band gap. This enables for greater use of the solar spectrum for photocatalysis, which results increase in degradation efficiency. The morphology of aluminium doped zinc oxide is hexagonal wurtzite [1]. Sulaiman S.A. Al Ghafry et al. noted that degradation efficiency of ZnO NPs is around 98.5% when it is doped with Ag, under solar light irradiation in 5hr. The band gap narrows from 3.6 to 3.19 eV [2]. Weiwei

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Han et. al., reported that the degradation efficiency of the ZnO nanocomposites increases to 98% when they are doped with Cr. The band gap is narrowed from 3.3 to 2.69 eV this enhances the visible light absorption capacity [3].

Hydrothermal method: Shadi Kohzadi et.al., reported that doping zinc oxide (ZnO) nanoparticles with molybdenum increases the degrading efficiency by 95% when measured under sunlight because molybdenum introduces free electrons into the ZnO lattice. These liberated electrons can act as catalysts for pollutant breakdown. Because molybdenum atoms introduce defects into the ZnO lattice, the bandgap of ZnO nanoparticles dropped from 3.67 eV to 2.8 eV. These defects operate as electron energy traps, lowering the energy required to jump from the valence band to the conduction band. As a result, the band gap is reduced [4]. M. Suresh et.al reported that degradation efficiency of Zinc oxide increased to 92% when nitrogen was doped into Zinc oxide under the presence of visible light. The bandgap of Zinc oxide is decreased from 3.16 to 3.03 eV when nitrogen was doped into it. The prepared Zinc oxide nano composite possesses a hexagonal wurtzite structure [5]. Manmohan et.al discovered that the degradation efficiency of Zinc oxide is increased to 98.5% when Neodymium (Nd) was doped into Zinc oxide in the presence of UV light. The study indicates that energy band gap of Nd doped ZnO sample was 3.19 eV while in case of ZnO sample 3.26 eV. Hexagonal rod shape morphology was observed in this analysis [6].

Ruijie Liu et.al reported that when Silver (Ag) doped into Zinc oxide (ZnO) the degradation efficiency of Zinc oxide increased to 97% in the presence of simulated sunlight. The band gap observed in ZnO nanocomposite is 3.1 eV when Silver was doped. The sample show the ZnO structure as hexagonal wurtzite [7]. Dhilleswara Rao Vaddi et al. discovered that when yttrium was doped into ZnO nano rods, the degradation efficiency improved to 96.8%, although the pure efficiency is 22% in the presence of visible light. With ZnO nanorods have a band gap of 2.779 eV with a hexagonal wurtzite shape [8]. Manmohan Lal et al. reported that the degrading efficiency of ZnO improves with increasing temperature, reaching 95% at 550^0 C under X-ray diffraction. Along with this, the band gap steadily lowers from 3.36 to 3.23 eV. When the temperature rises, the size of its hexagonal crystalline structure shrinks [9].

According to research by Zhenrui Yang et al., cobalt doping boosts the degradation efficiency of ZnO nanoparticles from 89% to 96% under visible light. Additionally, the bandgap is reduced from 3.37 to 2.81 eV [10]. Lina Hammed Mohammed et al. founded that the degradation efficiency of the Zno NPs was increased up to 86.98% in 90 min under sunlight irradiation, when it is doped with Co. The band gap narrowed from 3.31 to 3.12 eV which results in more absorption of sunlight [11]. R. Torkamani et al. found that all samples had a wurtzite structure, but the grain size of nanoparticles, nanorods, and thin film was smaller than that of the bulk sample. Nanoparticles had the smallest grain size, followed by nanorods and then thin film [12].

Auto-combustion method: Mahesha et.al observed that when Chromium is doped in Zinc oxide in the presence of visible light, the degradation efficiency increases to 95.4%. Chromium is a highly stable element, which means that it does not easily decay under the effect of light or heat. Chromium-doped ZnO is thus a more stable photocatalyst than undoped ZnO. The band gap has been reduced from 3.27 to 2.74 eV. The hexagonal wurtzite shape of chromium doped Zinc oxide is seen [13].

Simple combustion method: K. S. Mamatha et.al found out that when calcium is doped in zinc oxide in the presence of UV radiation, the degradation efficiency jumps to 90%. Calcium doping boosts ZnO's photoactivity, or its capacity to create electrons and holes in the presence of light. ZnO can absorb more photons and transform them into electrons and holes, which can subsequently be used to oxidize and destroy organic pollutants. When the fuel concentration is increased, the band gap of ZnO changes from 3.41 to 3.33 eV. The morphology of calcium doped Zinc oxide is hexagonal wurtzite, as discovered [14]. According to Irshad Ahmed et al., ZnO nanoparticle degrading efficiency increases to 95% in just 45 minutes when it is co-doped with Aluminum and Cobalt. The bandgap also decreases from 3.18 to 3.06 eV, and the particle size decreases from 13.26 to 11.88 nm [15]. Promod Kumar et al. reported that the degradation efficiency of the ZnO NPs is around 97% when it is doped Rb under natural sunlight irradiation. The band gap of ZnO was found to reduce from 3.2 to 2.97 eV after doping with Rb [16].

Co-precipitation: L. Anju Chanu et.al discovered that when zinc oxide is doped with gadolinium and exposed to UV light, the degradation efficiency increases to 96%. Electrons are trapped by Gd ions. This means that they

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can capture electrons produced by light absorption. This keeps electrons from recombining with holes, which is a primary cause of photocatalytic activity loss. The band gap has been reduced to 3.32 eV. When gadolinium is doped into zinc oxide, a hexagonal wurtzite structure is generated [17]. When copper (Cu) was doped into zinc oxide (ZnO), the degradation efficiency increased to 89.2% in the presence of sunlight, according to S. Sivakumar et al. The band gap was increased from 3.27 to 3.44 eV by doping copper in zinc oxide. Zinc oxide morphology was discovered to be spherical nano crystals [18]. M.A Kareem et al. discovered that when silver (Ag) was doped into zinc oxide in the presence of UV radiation, the degradation efficiency of the ZnO increased to 98%. The band gap of pure ZnO is 3.37, and the band gap is decreased to some amount once silver is doped into Zinc Oxide. Silver doped ZnO exhibited hexagonal wurtzite structure [19].

K. Janani Archana et al. noted that the degradation efficiency increased from 21% to 35% when Copper was doped into Zinc oxide in the presence of UV visible light. The bandgap was narrowed due to the doping. Spherical structure has been observed [20]. When cobalt was doped into zinc oxide while being observed by X-rays, Hui Pan et al. discovered that the degradation efficiency rose from 68% to 92%. The average size of the crystallite structure shrank with increasing doping concentration, as evidenced by the narrowing of the bandgap from 3.37 to 3.13 eV and the SEM results [21]. According to Muhammad Shahid Nadeem, when ZnO NPs are co-doped with Fe and Co, the bandgap decreases from 3.37 to 2.7 eV, and the efficiency rises to 98.8% in direct sunlight in 60 minutes [22]. Muhammad Azam Qamar et al. reported that degradation efficiency of 3d metal doped ZnO is Around 98% in 120 min under sunlight irradiations. It is also observed that the there is also a considerable reduction in band gap upto 2.50 eV [23].

According to Amel Muhson Naji et al., when ZnO NPs are combined with F and evaluated under the UV light spectrum, their degradation efficiency rises from 84% to 94% in 120 minutes. Additionally, the Band gap decreases from 3.37 to 2.13 eV [24]. Aaliya Ashpak Shaikh et al. reported that the degradation efficiency of ZnO NPs increases up to 98.5% in a time of 90 min, when it is doped with Ag, and it is observed under the UV light irradiation. The size of the nano particles decreases from 25.37 nm to 20.23 nm [25]. Amel Muhson Naji found that the degradation efficiency of F doped ZnO is 94% in 120 min compared to 40% for the pure ZnO. Narrowed bandgap energy (2.13 eV) contributed to the high degradation efficiency [26]. Baskaran Palanivel et al. reported that Co-doped ZnO with Gd and La exhibits the maximum degradation efficiency of 91% for Rh B and 74% for TCN under sunlight irradiation. The band gap narrowed from 3.16 to 2.42 eV [27].

III. METHODOLOGY

Cr doped $ZnFe_2O_4$ nanoparticles was prepared by a hydrothermal technique. Zinc nitrate hexahydrate, ferric nitrate dihydrate, chromium nitrates di hydrate, and sodium hydroxide of analytical grade were used to synthesize of Cr doped $ZnFe_2O_4$ nanoparticles. In this typical reaction procedure 2 mmol solution of zinc nitrate and 4 mmol of ferric nitrate are prepared with 25 ml of distilled water and 12 grams of sodium hydroxide is prepared with 50 ml of distilled water in separate beakers. A 0.06 mmol chromium nitrate solutions are prepared with 10 ml distilled water in separate beakers. Then the zinc nitrate is transferred into the burette and released drop vies into the ferric nitrate solution. This mixture was stirred vigorously for 30 minutes under magnetic stirrer. Later the doped solution (copper nitrate) is added to the above solution. Then the appropriate amount of NaOH was added to the mixture and the solution is magnetically stirred, set the value of pH between 11 to 12. Then the solution is transferred to a Teflon lined stainless steel autoclave. The autoclave was placed in a furnace held at temperature 180^{o}C for 12 h. After that the autoclave was allowed to cool to room temperature naturally, the resultant precipitate was centrifuged thrice with distilled water. After that the solution is allowed to dry naturally within the tubes and finally transferred into the incubator for complete dryness at temperature 100^{o}C for 5 h. Later the powder is grinded manually with the help of aged mortar for one hour to get the fine nano powder.

Sol-gel method:

Adriana Popa et.al noted that when ferrous ions in iron are doped into zinc oxide in the presence of UV light, the degradation efficiency increases to 97%. Zinc oxide has a comparatively high bandgap energy of 3.37 eV. This indicates that it takes a lot of UV light energy to excite electrons from the valence band to the conduction band. When ZnO is doped with ferrous ions, the band gap energy decreases to 2.9 eV, making electrons more easily excited for the photocatalysis reaction to occur. The morphology of the ZnO is found to be crystalline [28].

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Velumani Arun et al. found that Sn doped ZnO/Cds composites show 94% Photocatalytic degradation efficiency within 120 min under sunlight irradiation. It is also observered that the bandgap is narrowed [29]. Tahani M.

Bawazeer et al. found that the degradation efficiency of the ZnO NPs increases when it is doped with Fe and noticed that the particle size reduces from 23mm to 9mm. The band gap is reduced from 3.287 to 3.212 eV [30]. M. Costa-Silva et al. reported that the degradation efficiency of the ZnO NPs is around 81.3% when it is Co-doped with Ce-Ni under UV radiation. The band gap narrows after the doping [31].

Combustion synthesis method:

Raksha Umashankar et al. discovered that when copper was doped into zinc oxide nanoparticles under UV-visible light, the degradation efficiency increased to 94%. ZnO nanoparticles with a high surface area are produced by the combustion technique of synthesis. This is significant for photocatalysis because a large surface area allows the photocatalyst to interact with the pollutants more effectively. When copper was doped in zinc oxide, the band gap was reduced by 3.19 eV to 2.95 eV. Zinc oxide was discovered to have a hexagonal wurtzite structure [32]. Khadijah S. Al-Namshah reported that Co doping under UV light irradiation increased the decomposition efficiency of ZnO NPs to 91%. The bandgap value of ZnO is found to decrease from 3.27 eV to 2.81 eV upon Co doping [33].

Chemical precipitation method:

When Tin (Sn) was doped into Zinc oxide (ZnO), the breakdown efficiency of Zinc oxide improved to 96.52% in the presence of sunshine, according to S. Ragupathy et al. Electron traps are formed because of tin doping. Photo-generated electrons can be trapped by these electron traps, preventing them from recombining with holes. As a result, the concentration of photo-generated electrons increases, which can subsequently combine with organic contaminants to destroy them. During the doping process, the bandgap values steadily drop [34]. N. Siva et al. discovered that the ZnO nanoparticles' degrading efficiency rises when they are doped with Sn, and the bandgap narrows from 3.37 to 3.12 when observed under visible light [35]. Sabrina Roguai, Dr et al. noted that the degradation rate exceeds 90% for Fe-doped ZnO in 90 min while for undoped ZnO reaches Approximately 20% after a long time (120 min) under UV irradiation. The band gap also narrows by doping Fe [36].

Wet Chemical Approach:

Iqbal Ahmad et al. reported that Ni-doped ZnO photocatalysts showed a high degradation efficiency of MB, reaching 95% after 120 minutes of irradiation under X-ray diffraction. The photocatalysts were also stable and could be reused for multiple cycles without significant loss of activity [37]. According to research by V. Ganesh, when ZnO NPs are co-doped with Cu and Al, their degradation efficiency is around 88%, and their visible-light band gap also decreases from 3.30 to 3.26eV [38].

Green Synthesis method:

K. V Karthik et al. discovered that the degradation efficiency of the NPs increases from 60.7% to 90.1% when it is doped with Cu under the UV radiation. It is also observed that the band gap is narrowed from 3.31 to 2.8 eV [39].

Chemical Synthesis method:

A. Sridhar et al. noted that the degradation efficiency by Ag+Al Co-doped is 95% in 120 min compared to 57% of pure ZnO under the UV light irradiation. With increased in dopant concentration, the particle size was reduced from 41.15 nm to 19.51 nm. The band gap values showed a blue shift as the Al doping ratio increased [40].

IV. CONCLUSION

$ZnFe_2O_4$ and Cr doped $ZnFe_2O_4$ nanocomposite was synthesized by hydrothermal method. The prepared nano composite was characterized by using X-ray diffraction, energy dispersive X-ray spectroscopy attached scanning electron microscopy. Based on the results following conclusions are drawn.

1) The XRD patterns of $ZnFe_2O_4$ and Cr/ $ZnFe_2O_4$ nanocomposites are similar, indicating that the doping of Cr does not significantly affect the crystal structure of $ZnFe_2O_4$.
2) The average crystallite size of both pure $ZnFe_2O_4$ and Cr/ $ZnFe_2O_4$ nanocomposites are measured as 10 nm.

3) The SEM images show that the $ZnFe_2O_4$ and Cr/ $ZnFe_2O_4$ nanocomposites are spherical-shaped quantum dots and have a homogeneous distribution.

4) The EDX analysis confirms the presence of Zn, Fe, O, and Cr elements and purity of the $ZnFe_2O_4$ and Cr/ $ZnFe_2O_4$ nanocomposites.

5) The Cr/ $ZnFe_2O_4$ nanocomposites exhibit higher photocatalytic activity than the pure $ZnFe_2O_4$ nanocomposites for the degradation of RHB dye under visible light irradiation.

6) The photocatalytic degradation efficiency of the Cr/ $ZnFe_2O_4$ nanocomposites is 98% after 90 minutes of exposure, which is significantly higher than the 30% efficiency of the pure $ZnFe_2O_4$ nanocomposites.

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