Chapter 3

Recent Advancement on Ferrite Based Heterojunction for Photocatalytic Degradation of Organic Pollutants: A Review

Pooja Shandilya^{1*}, Shabnam Sambyal¹, Rohit Sharma¹, Amit Kumar^{2,3}, Dai-Viet N. Vo⁴

¹School of Advanced Chemical Sciences, Shoolini University, Solan, Himachal Pradesh, India-173229

²International Research Centre of Nanotechnology for Himalayan Sustainability (IRCNHS), Shoolini University, India

³College of Materials Science and Engineering, Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, Nanshan District Key Lab for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen 518055, PR China

⁴Center of Excellence for Green Energy and Environmental Nanomaterials (CE@GrEEN), Nguyen Tat Thanh University, 300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, 755414, Vietnam

*pooja@shooliniuniversity.com, poojashandil03@gmail.com

Abstract

The progress of ferrites and ferrites-based nanocomposites has become extensively popular in the field of photocatalytic wastewater treatment. This class of compound exhibit several fascinating properties related with their high stability, low cost, ease of functionalization, and biocompatibility. Ferrites carry outstanding magnetic behavior that helps in their easy recovery from the aqueous system thus reducing the cost. The morphology and various properties such as magnetic, absorption, optoelectronic of magnetic ferrites can be varied and optimize by applying different synthetic routes and reaction conditions. With this background we have briefly presented and reviewed the latest development in the field of photodegradation of aqueous pollutants using ferrites based heterojunction. Especially, the type-II, Z-scheme and S-scheme based heterojunction for enhanced pollutant degradation under the exposure of light are thoroughly describe. Ferrites have inherent potential in water remediation applications hence many examples were consider to impart valuable knowledge to the readers.

Nevertheless, the large-scale utilization of these magnetic nanoparticles still needs to be explored. Therefore, the gaps, challenges and future prospective of ferrites nanoparticles are also explained to unveil the un-scrutinized standard of ferrites nanoparticles.

Keywords

Ferrite Photocatalyst, Degradation, Heterojunction, Organic Pollutant, Z-Scheme, S-Scheme

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1. Introduction

Rapid population sprouting and industrialization have sparked serious impact on environment, human health and aquatic life. Various industries like cosmetic, pharmaceutical, rubber, paint, food, battery, textile mill and domestic waste dispensing harmful effluents directly into the ecosystem [1, 2]. These effluents carry innumerable toxic organic and inorganic substances, consuming accessible dissolved oxygen and deteriorate the quality of water. Therefore, it is an urgent need to develop sustainable and effective method to improve the water standard. Among different conventional (coagulation, precipitation, filtration, biodegradation), established (evaporation, oxidation, membrane separation, solvent extraction) and emerging (advanced oxidation, bio sorption, nanofiltration) technologies, heterogeneous photocatalysis based on advanced oxidation process is most successful due to its environment friendliness, cost effectiveness and less energy consumption [3-5]. The photocatalyst generally utilize the renewable solar energy to initiate and amplify the photochemical reactions. This process produces charge carrier which are responsible for redox reaction on photocatalytic surface. During the photocatalysis, the photogenerated h^+ react with water molecules to generate $\cdot OH$ radical possessing strong oxidative potential ($E^\circ = +2.34$ V vs NHE) sufficient for the degradation various kind of aqueous pollutants (Figure 1 a) [6-9].

As a photocatalyst, ferrite based material has drawn great interest and promptly became one of the hottest topics among scientist witnessed by the increase in number of publications per year from 2012 to 2021, Figure 1b. The ferrites are generally combination of most abundant element iron and oxygen. The most commonly used ferrites are Fe (II) oxides, Fe (III) oxides or Fe (II, III) oxides which present in different phases and crystal structures. For example, Fe (II, III) exhibits cubic structure whereas Fe (III) shows polymorphism mainly in four different phases which are α -Fe₂O₃, β -Fe₂O₃, γ -Fe₂O₃ and ε -Fe₂O₃. The ferrites can be fabricated through various synthetic method with distinct morphologies like nanoparticles, nanotubes, nano-spheres, nanowires, nanosheets etc. The typical ferrites generally show several advantageous features like superparamagnetic, high biocompatibility, ease of functionalization, optoelectronic tunability and high stability [10-11]. These outstanding properties of magnetic nano-ferrites paved special attention in environmental remediation via photodegradation. Liu et al. fabricated α -Fe₂O₃ via SDS-assisted grinding method showing Fenton like mechanism in the existence of H₂O₂ under visible irradiation and degraded 99.6% methylene blue (MB) in 40 minutes [12, 13]. Under visible irradiation reactive oxidation species (ROS) is generated responsible for photodegradation. The photoinduced electrons were captured by Fe³⁺ ions reducing it to Fe²⁺ ions to form Fenton reagent Fe²⁺/H₂O₂ that participate in photodegradation process.

For instance, Dhiman and co-workers fabricated ZnFe_2O_4 nanostructures via hydrothermal routes and studied for photodegradation of both cationic (safranin-O) in addition anionic remazol intense yellow) dye [14]. They controlled reaction conditions to prepared different morphologies like porous nanorods, nanoparticles, nano-flower and hollow microsphere of ZnFe_2O_4 and studied morphology based photocatalytic efficiency. The photocatalytic efficiency followed the order hollow microsphere ($115.23 \text{ m}^2\text{g}^{-1}$) < nano-flower ($92.73 \text{ m}^2\text{g}^{-1}$) < nanoparticles ($121.74 \text{ m}^2\text{g}^{-1}$) < porous nanorods ($138.43 \text{ m}^2\text{g}^{-1}$). These findings suggested that porous nanorods revealed maximum photodegradation activity toward both cationic and anionic dyes due to better distribution of charged species, high surface area and porous nature [15, 16]. Despite of different morphologies, ferrites nanoparticles also exhibit superparamagnetic, ferromagnetic or ferromagnetic characteristics. Among which superparamagnetic behaviour of ferrites are best for water purification on the note magnetic nanoparticles should possess high magnetization saturation and low value of coercivity and remanence magnetization. This is because superparamagnetic nanoparticles do not aggregate and can be dispersed freely in liquid medium even in absence of magnetic field. The magnetic behaviour shut off the use of tedious and lengthy process of centrifugation and filtration.

In photocatalysis, ferrites offer the additional advantages of high visible light absorption due to their narrow band gap of $\sim 2.0 \text{ eV}$ (Figure 1c) [17-30]. The narrow band-gap semiconductors suffer high recombination rate thus, heterojunction were constructed to facilitate the direction of charge migration. The p-n junction between CaFe_2O_4 and WO_3 nanocomposite for photocatalytic decomposition of acetaldehyde under visible irradiation were reported [31]. The low recombination rate of electron/hole pairs and high photocatalytic performance was detected due to the presence of internal electric field and bend bending induced at the interface of two different semiconductor materials. The presence of defect sites also helps in charge separation by trapping the electrons and allowing large number of potential charge species available for photo-oxidation and photoreduction of pollutants [32-35].

In this manuscript we have tried to present a comprehensive knowledge on the properties, synthetic techniques and photodegradation ability of ferrite base nanocomposite. We start with the introductory part elaborating the need of environment remediation technique, basic principle and role of photocatalysis in degradation and advantageous features of ferrites based nanomaterials. Then we have discussed the important properties of ferrites like magnetic, absorption, optoelectronic, targeted delivery and hyperthermia [36, 37]. Thereafter, various synthetic approach: hydrothermal, sol-gel citrate, chemical precipitation, conventional and other methods employed for the fabrication of nano-ferrites with various morphologies and dimensionality were considered. Finally, we have

discussed the usefulness of magnetic separable nanomaterials in photocatalytic degradation of organic pollutants for wastewater treatment. We have briefly lit up the various heterojunction type-II, Z-scheme and S-scheme based photocatalyst validating high photo-efficiency. In conclusion the various gaps, challenges and future prospective of ferrites based heterojunction were explicate.

Figure 1: (a) General mechanism of photodegradation [6] (b) Reported publication of ferrites in last 10 years source of information <https://www.sciencedirect.com> by using keywords “Ferrites in photodegradation” (c) Band gap values of spinel ferrites and cations substituting ferrites [17-30].

2. Properties

2.1 Magnetic property

Strong magnetic behavior of ferrite is one of the most important functional characteristics responsible for easy, economical and selective separation. The magnetic separation is superior to other conventional techniques like centrifugation and filtration. The magnetism in ferrites is affected by several factors like oxidation state and distribution of cations, electronic configuration between octahedral and tetrahedral sites within the crystal lattice. Additionally, fabrication process, crystallinity, size and surface or interface effect also influence magnetic properties by changing the saturation magnetization (M_s), coercivity (H_c) and remanent magnetization (M_r) [38]. The use of complex fabrication method thermal decomposition or hydrothermal accompanied non-uniform distribution of cations in ferrites. While the deposition or solid-state reaction provides high inversion degree to nanoparticles in ferrites like their bulk counterpart [39].

In 2017, Li and co-workers gave the correlation between particle size and magnetic performance of Fe_3O_4 nanoparticles [40]. It was found with increase in particle size the M_s increase without affecting shape or crystallinity of particles. Whereas, the other parameters like M_r and H_c are influenced by particle size and reached maximum value of 13 emu/g and 190 Oe, respectively when particle size reached to 76 nm. The further increase in particle size changes the cubic structure from single domain to multi-domain and also reduces the M_r and H_c value. Eventually, H_c and M_r calculated for sphere like Fe_2O_3 nanoparticles was smaller than cube like nanoparticles. These findings clearly demonstrated that special attention needs to be given in crystalline properties and size of nanoparticles in order to obtain satisfactory magnetic performance. Although, ferrites in bulk-phase remains in multi-domains structure but when size decreased to 15-100 nm, ferrites nanoparticles possessed single domain structure with superparamagnetic behavior where the atomic spin aligned in same direction. In contrary to other conventional paramagnetic materials single domain Fe_2O_3 do not possess any residual magnetic moment in the absence of an external applied field. This unique feature guarantee ferrite nanoparticles to be outstanding in various biomedical and industrial fields. Besides this magnetic anisotropy related with chemical composition, cation distribution or symmetry of interstitial positions is also contributed to effectively enhance or tailored magnetic characteristics of ferrites.

2.2 Absorption property

Absorption is one of the highly potential physical treatment method to eliminate various organic and inorganic pollutant from waste water. This technique involves the attachment

of organic or inorganic contaminant on the absorbent surface in order to carry out the mineralization process. However, absorption capacity of ferrites is much less as compare to other carbon-based adsorbent like graphene or activated carbon. However, by controlling the synthetic approach, morphology, size, chemical composition of ferrites, the sorption kinetics and absorption efficiency of ferrites can be modified. Generally, the absorption mechanism of ferrites nanoparticles depends upon several factors including electrostatic interaction, π - π interaction, hydrogen bonding, ion exchange, chemisorption, surface complexation and formation of new bonds. The surface of ferrites possesses large number of hydroxyl groups (Fe-OH) which are considered as crucial binding sites for various pollutants. Thus, by altering the density of these hydroxyl binding sites and their availability for adsorbate through various techniques, the absorption capacity found to be increase exceptionally [38, 41]. For example, Ahalya et al. doped manganese ferrite (MnFe_2O_4) with different concentration of cobalt ions ($\text{Co}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$) [42]. The highest absorption capacity was observed for the absorption of Cr (VI) at $x=0.6$ due to increase in size and crystalline nature of nanoparticles. Further increase in dopant concentration, form more CoFe_2O_4 phases which have less absorption capacity than MnFe_2O_4 .

Also, Ni-Zn ferrites fabricated by sol-gel method were used for efficient removal of Congo red dye at room temperature [43]. The absorption mechanism of doped nano-ferrites could be explained by ion exchange process. When the ferrites are doped with different metals ions, it affected the crystallinity, size, inter planner spacing and concentration of free electrons in crystal lattice due to difference in size of doped metal and parent metal cations. This modifies the absorption capacity of doped nano-ferrites. Interestingly, free electrons present in crystal lattice decrease the oxidation state of pollutant, and thereby successively increase the magnitude of absorption (Figure 2a). Apart from this polymer or surfactant coating are also well known strategies to enhance absorption ability of ferrite nanoparticles beneficial in pollutant degradation [44, 45]. During the surface coating single or double-layer formation occur on ferrite surface by long chain compound containing different functional groups. These reactive function group represents active sites for adhesion of various pollutant on surface of nano-ferrites. Beside, these functional groups in polymer matrix also act as potential binding sites for the adsorptional removal of pollutants (Figure 2b).

2.3 Optoelectronic property

Optoelectronic property is a basic characteristic of semiconducting materials based on quantum mechanical effects of light on the electronic system. Being a promising semiconductor, ferrites have achieved special attention in photocatalysis and sensor applications due to their optoelectronic tunability, high stability, high charge density,

highly abundant and cost-effectiveness. The band-gap value of spinel ferrites nanoparticles approximately lies between 1.4 to 2.7 eV depending upon the type of cations present in the nanostructure. This feature of ferrites is highly promising in the field of photocatalysis. On irradiation, the photogenerated charge carrier directly participate in generation of superoxide and hydroxyl radical species. These reactive species owns high redox potential and therefore, easily degrade large number of pollutants. Despite of several advantageous optoelectronic feature, ferrites bear high recombination rate and low specific surface area. Therefore, different modification strategies like heterojunction formation, morphological modification, doping have been explored to increase density of active sites and reduce the diffusion length. These modifications increase the separation of charge carriers and increase their accessibility for surface reactions [46, 47].

Recently, Kang and groups constructed $\text{Fe}_2\text{O}_3/\text{C-g-C}_3\text{N}_4$ based Z-scheme photocatalyst for degradation of rhodamine B [48]. It was observed through various studies that electron-hole recombination was remarkably suppressed after heterojunction formation. In $\text{Fe}_2\text{O}_3/\text{C-g-C}_3\text{N}_4$ photocatalyst, the VB holes of Fe_2O_3 transport to VB of g- C_3N_4 . Whereas, photogenerated electrons migrated from CB of Fe_2O_3 to CB of g- C_3N_4 . This causes recombination of useless charge carrier while photoexcited electrons and holes with high redox potential are available for photodegradation process. Similarly, Huo et al. synthesized Z-scheme based $\alpha\text{-Fe}_2\text{O}_3/\text{MIL-101 (Cr)}$ hybrid for complete removal of carbamazepine in the presence of visible illumination [49]. The photogenerated carriers efficiently separated by Z-scheme pathway minimizing recombination rate and maximized photodegradation performance. These findings suggested that the optoelectronic properties of ferrites could be improved by various technique which enhance their usability in photocatalysis.

2.4 Targeted delivery properties

The target specific drug delivery is a novel and beneficial approach in the field of nanomedicine. These properties were established on the magnetic behavior of substances, therefore owing to their superparamagnetic characteristic's ferrites are considered as potential candidate for target specific drug delivery application. The direction and orientation of these substances could be controlled by applying an external magnetic field. The other specific feature of ferrites like high chemical stability, large number of active sites tunable size and shape and choices in functionalization make them highly suitable for targeted delivery [50]. For instance, Maiti et al. fabricated surface functionalized multifunctional ZnFe_2O_4 as a drug carrier for hydrophilic and hydrophobic anti-cancer drug molecules namely Daunorubicin and Curcumin, respectively [51]. It was

observed that ZnFe_2O_4 proved excellent carrier for both kind of drugs and displayed high efficacy for targeting and damaging harmful cancer cells (HeLa).

In general, the release of drugs from their carriers at specific sites depending upon various external stimulus (magnetic field, temperature, presence of light and ultrasound) and internal stimulus (pH or presence of enzyme). Thus, target specific drug delivery by magnetic nanoparticles is becoming beneficial in several ways as it improves pharmacokinetic and pharmacodynamics profile of drugs, intensify drug stability and aqueous solubility and reduces toxic effect and drug concentration in non-targeted tissues. Also, the biocompatibility, biodegradability and non-toxicity along with easy navigation via applied magnetic field, the magnetic nanoparticles have explored in various applications like magnetic resonance imaging, hyperthermia and magnetofection [52].

2.5 Hyperthermia properties

Generally, hyperthermia signifies the overheating conditions, when temperature of the system is raised above normal temperature. The ferrites nanoparticles possessed magnetic hyperthermia properties in which the electromagnetic energy is converted into heat energy via energy dissipation under the effect of alternating current magnetic field. The two types of relaxation process contribute in the energy dissipation of magnetic nanoparticles called Brown relaxation and Neel relaxation. Hyperthermia is a promising approach for the treatment of cancerous cells where specific tissue or organ for tumor therapy is heated to 41-46 °C with the help of laser wavelength, microwave or radio frequency. Since, the tumor cells show low thermal resistance due to poor development of blood vessels as compared to healthy tissue which mark hyperthermia a very successful approach for curing cancer. However, during the whole body and regional hyperthermia few clinical side effects were also observed by healthy tissues. Therefore, ferrites can be used to resolve this issue as it provides localized hyperthermia which only heat up the tumor zone. The magnetic ferrites nanoparticles not only demonstrate localized hyperthermia effect but also supplies control over the release kinetic of drugs and consequently proved fascinating compound in cancer treatment [53, 54]. For instance, Ebrahimisadr et al. examined the effect of concentration of Fe_2O_3 nanoparticles on the hyperthermia property and observe the maximum temperature reaches to 58 °C when concentration of nanoparticles is 12.5%. At the same time when concentration decreases to 1% in suspension, hyperthermia effect also reduces and temperature raised to 9 °C only (Figure. 2 c). These finding concludes that heat generation effect increased with increase in concentration. Whereas no significant effects of change in concentration were observed on specific absorption rate value. This result displayed that magnetic

energy dissipation or specific absorption rate of ferrofluid are independent of concentration (Figure 2 d).

3. Synthesis

The ferrite nanocomposite fabricated by different synthetic methods regulate the size, shape, aspect ratio orientation, surface area, stability and purity. The diverse morphologies, surface area and porosity obtained through different synthetic routes: hydrothermal, precipitation, sol-gel, thermal decomposition and microwave assisted method are beneficial in various photocatalytic applications. Hence, proper synthetic techniques must be applied to deliver desired morphology with high yield. Also, cost effective, mild reaction conditions and most importantly green synthesis of ferrites should be the requisite.

3.1 Hydrothermal method

Hydrothermal process operated under high temperature and pressure is environmental-friendly method for large production of ferrites nanomaterials [55]. The various factors like precursor, pH, temperature, reactant concentration and additives are applied for dispersion and crystal morphology. Wu and groups synthesized g-C₃N₄/CuFe₂O₃ with Fe-Ni by hydrothermal method to remove arsenate from water [56]. The pH and temperature show great impact on shape and size of nanostructure. Surface morphology of nanocomposite examined by SEM in which Fe-Ni foam substance possess smooth surface (Figure 3a). The Cu present in the form of Cu₂Fe₂O₄, mass of Cu₂Fe₂O₄ on Fe-Ni depends upon stoichiometric relationship between Cu₂Fe₂O₄ and Cu. Therefore, nanocomposite substance shows higher activity which attributed to efficient charge separation. In another study BiFe₂O₃ were fabricated by using Bi(NO₃)₃.5H₂O and Fe(NO₃)₃.9H₂O precursor by adding KOH solution that assist in co-precipitation of Bi³⁺ and Fe³⁺ ions [57]. While, increase concentration of KOH converts the irregular structure (2.7µm) to brick like (2.6µm) of BiFe₂O₃. Also, particle size has a great impact on photocatalytic activity, smaller nanoparticles exhibit higher efficiency against methyl orange. NiFe₂O₄/BiPO₄ nanocomposite degraded 98% of tetracycline and 99% of rhodamine-B [58, 59]. The obtained heterostructure attain tiny particle size, pore volume and large specific surface area. The large surface area accountable by huge active sites determined by BET isotherm. From Figure 3b shows pore size distribution of BiPO₄ nanorods on NiFe₂O₄ nanoplates, the BET area increases with BiPO₄ substance and exhibiting high surface area 24.1085m²/g in NiFe₂O₄/BiPO₄. From the discussion, we can conclude that hydrothermal method is a suitable for optimizing the particle size of ferrites nanoparticle in such a way so as to accomplish higher photocatalytic efficiency.

Sol-gel process comprise with addition of metal precursor with citric acid to form gel. Precursor dissolved in ethanol and water at pH 9 until gel solution is formed afterward

the gel dried at 450-800°C. Golshan et al., prepared $\text{TiO}_2@\text{CuFe}_2\text{O}_4$ by sol-gel method and determine the crystal phase structure of photocatalyst by XRD [60]. Different diffraction pattern of crystal structure with variety of crystal lattice were shown in Figure 3c. Different ferrite have dissimilar diffraction pattern due to metal cation of varied size giving different spectrum. The similar pattern of diffraction peak of TiO_2 and CuFe_2O_4 shows high purity whereas, strong and narrow diffraction peak of $\text{TiO}_2@\text{CuFe}_2\text{O}_4$ signifies excellent crystalline degree. Mg doped Co- Fe_2O_3 nanocomposite synthesized by auto-combustion process whose magnetic hysteresis curve analyzed at room temperature [61]. Magnetic parameter for instance coercivity, magnetization and remanence were examined by increasing Mg concentration in Co- Fe_2O_4 . The saturation magnetization for Co and Mg ferrite were 77.94emu/g and 35.22emu/g. As mentioned, Neel model magnetization of tetrahedral sub-lattice was anti-parallel to octahedral. Although, Mg doped ferrites, non-magnetic Co^{2+} and Mg^{2+} ion to increase magnetic moment and Mg^{2+} ion having octahedral sites (Figure 3d). Many researchers are curious on knowing the influence of temperature and calcination time on photocatalytic mechanism.

3.3 Chemical-precipitation method

Chemical co-precipitation is used to fabricate ferrites by same mixing metal in aqueous solution with the addition of surfactant followed by thermal treatment. The pH is maintained at 7-10 so as to precipitate ferrite nanoparticle and then calcined at high temperature. Ternary $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2/\text{Ag}/\text{AgFeO}_2$ nanocomposite fabricated by in-situ deposition-precipitation method in the presence of ethanol reducing Ag^+ to Ag^0 (Figure 3e). The heterostructure generate ROS to carry out the degradation of tetracycline [62]. X-ray photoelectron spectrum examined chemical state and surface elemental composition. Additionally, weight percentage of each species analyzed on the basis of atomic concentration of elements. Besides, heterostructure having Bi, Cl show negative shift and Ag, Fe exhibit positive movement in XPS. The strong interaction between AgFeO_2 and $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ assist in electron migration from AgFeO_2 to $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ surface. Further, Ni doped CoFe_2O_3 nanocomposite was fabricated by chemical co-precipitation method applied for the degradation of organic dye [63]. The scanning electron microscopy (SEM) studied morphology of surface and surface coated microstructure. SEM shows irregular morphology due to distorted crystalline structure and having porous nature (Figure 3f). The pH exhibit important role on crystalline structure with little effect on composition of substance. As nickel ions added in cobalt ferrite, it alters the lattice parameter.

Figure 3: (a) TEM images of $\text{CuFe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ [56] (b) pore-size determination with various sample of BiPO_4 and NiFe_2O_3 [58] (c) XRD spectra of CuFe_2O_3 , $\text{NiFe}_2\text{O}_3@/\text{TiO}_2$ and TiO_2 [61] (d) hysteresis loop of $\text{Co}_{1-x}\text{MgFe}_2\text{O}_4$ [61] (e) XPS spectra of AgFeO_2 [62] (f) SEM images of $\text{Ni-CoFe}_2\text{O}_3$ [63].

3.4 Conventional solid-state method

In solid state technique powders of metal salt and iron for instance Fe_2O_3 , CaFe_2O_4 , and CaCO_3 are heated up to 1100°C . Spinel ferrites MFe_2O_4 ($\text{M} = \text{Zn}$, Cd and Mg) along with Fe^{3+} in d^5 electron configuration can be synthesized through solid state mechanism [64]. For spinel compound crystallographic cationic sites are tetrahedral and octahedral in nature. The photodegradation of acetic acid liberate enormous amount of CO_2 under xenon lamp (300W). Before the reaction pH of aqueous solution was at 2.4 and remain constant throughout the reaction. Further, Cd doped Zn ferrite ($\text{Co}_{0.5}\text{ZnO}_{0.5}\text{Cd}_{0.2}\text{Fe}_{1.8}\text{O}_4$) synthesized by providing different calcination temperature [65]. Nanocomposite were fabricated by low-cost solid state reaction process and calcinated at high temperature (Figure 4a). While increasing temperature up to 1000°C lattice cell dimension increases by decreasing micro-strain. The cubic crystalline structure of nanoparticle identifies by Williamson and Hall size and strain broadening. Though, broadening of peak with additive component possess distinct θ value depending on the size and strain. From size strain the isotropic and micro contribution can be determined whereas, value of constant

(K) depend upon shape of crystal. However, this method has many benefits such as good crystallinity, simple synthesis still bear certain limitation of large particle size along with the formation of additional undesirable phase.

3.5 Other method

Various other methods such as combustion, electro-spinning and poly-condensation method have also been describe for the synthesis of ferrites nanocomposite. The simple, fine homogenous Mn-Zn ferrites nanoparticle co-doped with Sm^{3+} - Gd^{3+} ion synthesize by combustion method possess effective magnetic, structural, and electrical properties [66]. Addition of co-doped ion increases crystalline structure, saturation magnetization and tunable electrical property. Based on the fact the production of porous substance suitable for catalyst-based or thermal insulation application. Electro-spinning method was used to prepare CoFe_2O_4 , with metal nitrate precursor, polymeric carrier and PVP [67]. The magnetic property of magnetic fibers are related to substitution ion and thermal temperature. In addition, three-dimensional ferrite prepared by one step ultrasonic spray pyrolysis by using sulfonated polystyrene as sacrificial reagent [68]. Acetone plays important role by increasing selectivity and stability of structure with active sites. The N_2 adsorption-desorption isotherm exhibiting relative pressure (P/P_0) (0.2-1.0) shows porous like structure. Mesoporous formation with pore size less than 20 nm ascribed to particle packing and outgassing due to decomposition of sphere templates (Figure 4b). It is known that refractory substance prepared by using self-propagating high temperature combustion process. Zhao et al., synthesized $\text{NiFe}_2\text{O}_4/\text{Ag}_3\text{PO}_4$ nanoparticle fabricated by ion-exchange technique by adding amount of Ag-ammonia and NiFe_2O_4 solution [69]. In the synthesis, nanoparticle was withdrawn at regular interval and filtered through membrane to remove the photocatalyst. It comprises of agglomerated grain with irregular, spherical structure with diameter 2.5 mm and NiFe_2O_4 diameter 2 mm (Figure 4c). Correspondingly, g- $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_3$ fabricated through poly-condensation of urea at temperature up to 550 °C [70]. From Figure 4d EDX spectra indicate the presence of Ni, Fe C, N and O comprise of g- $\text{C}_3\text{N}_4/\text{NiFe}_2\text{O}_3$.

Figure 4: (a) Synthetic method of ferrite particles [65] (b) Pore size determination of 3D ZnFe₂O₃ MPs [68] (c) SEM images of Ag₃PO₄/NiFe₂O₄ [69] (d) EDX spectra of GCN/NiFe₂O₄ [70].

4. Application in photodegradation

4.1 Bare and doped ferrite

Spinel ferrite nanocomposite NiFe₂O₄, ZnFe₂O₄, SnFe₂O₄ and CoFe₂O₄ have shown strong visible light activity, magnetic recyclability, non-toxicity, low cost, and environment friendly [71,72]. Among metal oxide semiconductor, Fe₂O₃ considered as stable semiconductor for photocatalytic reaction due to low band-gap (2.3eV), recyclability, earth abundant high harvesting light and excellent stability. In photocatalytic mechanism of Zn ferrites-based heterojunction, photo-illuminated electron is migrated to CB reducing Fe³⁺ to Fe²⁺ also generating ·SO₄²⁻ on CB and ·OH radicals at VB (Figure 5a) [71]. As pH is 6 total organic carbon and chemical oxygen demand is 50.5% and 78.6% in 300 min. Zn doped in cobalt ferrite material studied by diffraction peak shift towards lower range [73]. The absorption peak at 232 nm is ascribed to Fe³⁺ and O charge migration in octahedral coordination (Figure 5 b). Absorbance band at 300 nm arises due to the charge migration between oxygen and cobalt in tetrahedral sites and band at 477 and 627nm indicates Co²⁺ and Fe³⁺ ion in tetrahedral and octahedral geometry. In cobalt doped ZnFe₂O₃, valance band edge present at 0.38eV and CB edge at

2.43eV but in Co doped Fe_2O_3 CB edge was less negative than that of redox potential of O_2 (-0.33 V). Therefore, electron in CB do not generate $\cdot\text{O}_2^-$ while, electron in CB of cobalt doped ZnFe_2O_3 react with H_2O_2 to generate $\cdot\text{OH}$ radical (Figure 5c).

The doping in ferrites suppress the recombination rate of charges and lowers the luminescence intensity. Despite of huge accomplishment ferrites as single component does not have acceptable performance. This is due to rapid recombination of charge carrier and small hole dispersion distance of around 2-4 nm. The various modification is required to enhance surface area, number of active sites, promote photoefficiency and reduce recombination. Different support material were utilized to magnify adsorptional ability by increasing surface area and to improve thermal and chemical stability. The various support material such as SiO_2 , g- C_3N_4 , carbon nanotubes, graphene, graphene aerogel, carbon quantum dots, metal organic framework were used. These support material may assist in reducing the agglomeration of nanoparticles and behave as electron scavenger thereby minimizing recombination process. It also provide additional adsorption site for pollutant and improves the absorption range of photocatalyst apart, good support material also prevent the formation of inappropriate heterojunction. Moreover, heterojunction construction for outstanding performance can be an effective approach to enhance photocatalytic efficiency and discussed in next segment.

4.2 Type-II based ferrite heterojunction

Heterojunction construction appears to be an effective strategy to simultaneously utilize high redox potential and broad absorption range which is merely not possible in either bare or doped photocatalysts. To date, numerous type-II based ferrite heterojunction were constructed to enhance photocatalytic activity. The ferromagnetic NiFe_2O_4 with antiparallel spin between Ni^{2+} and Fe^{3+} ions present at octahedral and tetrahedral sites, respectively possess an inverse spinel structure. NiFe_2O_4 a narrow band gap semiconductor exhibit broad absorption range beneficial for photocatalytic processes. The visible light driven $\text{NiFe}_2\text{O}_4/\text{Bi}_2\text{O}_3$ nanocomposite used for antibiotic tetracycline degradation fabricated by microwave-assisted hydrothermal method [74]. The suitable band potential value where, photogenerated electron in CB of NiFe_2O_4 were transfer to CB of Bi_2O_3 due to more negative CB of NiFe_2O_4 than Bi_2O_3 that suppress the recombination rate of charges at the interface (Figure 5d).

From UV absorption NiFe_2O_4 display sharp absorption edge at 750 nm whereas, the heterojunction exhibit absorption range of 430-600 nm, corresponds to the band-gap of 1.70eV (NiFe_2O_4), 2.80eV (Bi_2O_3) and 1.67eV ($\text{NiFe}_2\text{O}_4/\text{Bi}_2\text{O}_3$) heterojunction. Bare NiFe_2O_4 degraded 47% of antibiotic whereas, degradation efficiency reaches to 90% in min in the presence of heterostructure with 50% of NiFe_2O_4 . Increasing the concentration

of NiFe_2O_4 above 50% may be due to the increased recombination rate. The degradation efficiency was further confirmed by determining total organic carbon (TOC) which is nearly 52% in 90 min. This confirms the mineralization of tetracycline into CO_2 and H_2O molecule. Further, the role of main active species is realized by performing scavenging experiment. The EDTA and isopropyl alcohol were added as holes, $\cdot\text{OH}$ radical scavenger. The percentage of degradation reaches to 65% and 89% with the addition of holes and $\cdot\text{OH}$ radical scavengers. The obtained results validate the role of holes as main active species in photodegradation.

CdS quantum dots decorated by $\text{CaFe}_2\text{O}_4@\text{ZnFe}_2\text{O}_4$ prepared by sol-gel auto combustion followed by deposition method and 83% of norfloxacin photodegraded in 90 min under solar irradiation [75]. The maximum degradation was noticed at pH=3, at this pH norfloxacin exists as positively charged species whereas, at this pH heterojunction surface is negatively charged about -12.07 mV as confirmed by zeta potential analysis. The heterojunction formation was established by band bending (Fig 5e and f) where, the band edge potential and Fermi level was calculated by equation 1 so as to convert normal hydrogen electrode value to vacuum energy level.

$$E_{NHE} = -4.5 - E_{vac} \quad (1)$$

The work function is related to work function and vacuum energy level by equation 2.

$$\phi = E_{vac} - E_F \quad (2)$$

After heterojunction formation, the band edges of ZnFe_2O_4 bend by 1.63 eV while the band structure of p-type CaFe_2O_4 remains intact. This band bending directs the charge transfer in one direction called iso-energetic electron transfer. The iso-energetic electron transfer between CdS and CaFe_2O_4 where, the electrons and holes migrate from CB and VB CdS to the CB and VB of CaFe_2O_4 , respectively. The obtained results were also supported by enhanced photocurrent density from 5.9 to 10.39 mA/cm^2 . Generally, charge transfer mechanism is based upon coulombic interaction at the interface of donor and acceptor semiconductor. However, charge transfer pathway in this ternary heterojunction is claimed to happen via iso-energetic electron transfer. The enhanced interfacial charge transfer significantly reduces recombination by increasing lifetime of charge carriers. Here, h^+ and $\cdot\text{O}_2^-$ is the major active species however, outstanding degradation was observed with $\cdot\text{SO}_4^-$ radical. The development of heterojunction especially type-II attracts great interest of most of the researcher, nowadays it still having

some drawbacks. Even through kinetics point of view electron transferred from SC2 to SC1 was blocked by electrostatic repulsions between CB of two heterojunction, holes migrated from SC1 to SC2 prohibited by same repulsion between their holes. Simultaneously, thermodynamic, formation of type-II heterojunction minimizes the redox potential of photocatalyst, reduce photocatalytic reaction.

Figure 5: (a) Photo-degradation structure of ZnFe_2O_3 [71] (b) Schematic diagram of CZF4 [73] (c) UV-vis absorption spectra of different CZF5 samples [73] (d) Charge migration mechanism of Bi_2O_3 and NiFe_2O_4 [74] (e) Band bending mechanism in $\text{CaFe}_2\text{O}_4@/\text{ZnFe}_2\text{O}_4$ -heterojunction (f) Iso-energetic charge transfer in $\text{CdS}/\text{CaFe}_2\text{O}_4@/\text{ZnFe}_2\text{O}_4$ [75].

4.3 Z-scheme based ferrite heterojunction

Z-scheme based heterojunction attract great attention due to their enhance photoefficiency, high charge separation owing to directional migration of charge carrier, and high reduction and oxidation ability. For the comprehensive understanding of Z-scheme heterojunction, its historical development from 1st generation to recent 3rd generation must be explore in detail (Figure 6) [76]. Firstly, Bard et al. in 1979 proposed

the concept of Z-scheme [77]. The three generation comprise of (i) Traditional Z-scheme, (ii) All-solid-state Z-scheme, and (iii) Direct Z-scheme. The traditional Z-scheme also called liquid-phase Z-scheme the two semiconductor are combine with reversible redox mediator ($\text{Fe}^{3+}/\text{Fe}^{2+}$ and IO_3^-/I^-). The redox ion pair facilitates the transfer of electrons from the CB of SC-II to the VB of SC-I thereby recombining the futile electron-hole pair. In this manner, electron and holes remain with the SC-I and SC-II with higher reduction and oxidation potential, respectively. The 1st generation of Z-scheme limits due to the reversible nature of redox ion pair hence both reduction and oxidation will compete with each other and reducing the photo-conversion efficiency. Moreover, it is only applicable in liquid phase that limits its implementation in other phases.

The 2nd generation, all-solid-state Z-scheme proposed in 2006 by Tada and group [78]. This generation have noble metal (Au and Ag) as electron mediator instead of reversible redox mediator therefore, it greatly inhibit the backward reaction. Though, employing rare noble metal is not a cost-effective technique consequently cannot be applied to large-scale. However, light shielding effect of redox and electron mediator in both 1st and 2nd generation greatly reduce the light absorption ability of photocatalyst. In 3rd generation of Z-scheme the two semiconductor are in direct contact with each other where, the charge migration is driven by the generation of internal electric field at the interface [79]. Direct Z-scheme completely inherit all the advantages of 1st and 2nd generation such as efficient charge separation, utilization of band edges with high redox potential. Owing to the various advantages direct Z-scheme heterojunction has been widely explored.

Figure 6: Hierarchy of the progression in Z-scheme heterojunction from 1st generation to 3rd generation.

The development of Z-scheme encouraged various researchers for the fabrication of ferrite based photocatalytic system. Liu and co-worker utilized simple hydrothermal method for the preparation of ZnS/Fe₂O₃/GO [80]. It reveals that heterojunction photodegraded 96% and 90% of MB in 40 and 480 min under UV light and visible light, respectively. The obtained results ascribed to excellent light harvesting ability, large surface area, enhanced interfacial charge separation and low charge migration resistance. ZnS quantum dots exhibit quantum confinement which is responsible for its optical and electronic properties and hence beneficial for photocatalytic application. Here, graphene oxide act as supportive material for ZnS QDs and Fe₂O₃ nanoparticles so as to minimize the agglomeration thereby surface area remains intact. Apart, GO also act as electron mediator and making charge migration process more facile. The surface modification of ZnS and Fe₂O₃ were done by using thioglycolic acid (-COOH) and citric acid ((-OH) containing so as to covalently bind both ZnS and Fe₂O₃ together. The photocatalytic mechanism involves the recombination of photogenerated electron from CB of Fe₂O₃ to VB of ZnS. The electron in the CB of ZnS reduces O₂ to generate $\cdot\text{O}_2^-$ radical meanwhile, VB holes on Fe₂O₃ oxidize H₂O molecule to generate $\cdot\text{OH}$ radical (Figure 7a). The heterojunction is easily separable within 95s under magnetic field.

Wang and groups fabricated nanorods g-C₃N₄/Fe₂O₃ heterojunction with addition of Fe-melamine supra-molecular act as sacrificial template [81]. The structure of metal organic supramolecular network made by alternating ligand, metal and fabrication condition like solvent, ligands, temperature, and molar ratio of metal ions. g-C₃N₄ nanoparticle attract wide attention due to high photochemical stability and good electronic structure. The high specific surface area of Fe₂O₃/g-C₃N₄ (11.96m²g⁻¹) is reported than bare g-C₃N₄ (5.2m²g⁻¹) as examined by adsorption isotherm. It was observed that heterostructure completely degrade RhB in 20 min in comparison to g-C₃N₄ which degraded only 20% of dye.

NiFe₂O₄/BiPO₄ heterojunction were synthesized via hydrothermal method in which 1D BiPO₄ nanorods anchored on NiFe₂O₄ nanoplates [82]. The constructed 1D and 2D heterojunction degraded 99% and 98% of RhB and TC in 100 and 60 min, respectively. From trapping experiment, number of scavenger reagent like tert-butanol, isopropanol for $\cdot\text{OH}$, ammonium oxalate (AO), triethanolamine (TEOA), ethylenediaminetetraacetic acid (EDTA) for h⁺ and benzoquinone (BQ) for $\cdot\text{O}_2^-$ can be used. On adding TEOA (90%) high degradation efficiency is achieved whereas, on addition of IPA and BQ the photodegradation efficiency was decreased up to 45% and 51% respectively (Figure 7b). Besides, radical trapping test $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radical were active species and the direction of charge migration verified Z-scheme mechanism.

It was recently reported that, highly magnetic double Z-scheme $\text{Fe}_2\text{O}_3@\text{NiFe}_2\text{O}_3/\text{P-g-C}_3\text{N}_4$, fabricated by co-precipitation method followed by calcination at 400°C [83]. The low cost, metal free and eco-friendly heterojunction degraded 90% of CIP under visible light. In inverse spinel, the Ni^{2+} and Fe^{3+} ions in octahedral sites and tetrahedral sites with antiparallel spins produce ferrimagnetism. The $\text{Fe}_3\text{O}_4@\text{NiFe}_2\text{O}_3/\text{P-g-C}_3\text{N}_4$ heterojunction have dual Z-scheme mechanism, one Z-scheme exist between NiFe_2O_3 and $\text{P-g-C}_3\text{N}_4$ while another one operates between Fe_3O_4 and NiFe_2O_3 (Figure 7c). Further, the flat band potential and type of semiconductor can be confirmed by Mott-schottky plot where, the positive MS plot represent n-type semiconductor and negative MS plot represent p-type. As mentioned in this research article the value for NiFe_2O_3 , $\text{P-g-C}_3\text{N}_4$ and Fe_3O_4 is +1.54, -1.47 and -0.6 V w.r.t. Ag/AgCl electrode. The shifting of holes from Ni^{3+} to Ni^{2+} responsible for p-type behaviour. Similarly, transfer of electron from Fe^{2+} to Fe^{3+} impart n-type nature to Fe_3O_4 . Linear-sweep voltammetry (LSV) display charge separation efficiency analysed by photocurrent densities. On illuminating Fe_3O_4 surface with light, it generates anodic current of 1.377 mAcm^{-2} confirming n-type behaviour Figure 7d. The heterojunction under positive bias potential of +1.5 V display sharp rise in photocurrent density to 1.87 mAcm^{-2} . The integrated synergistic effect of bare semiconductor enhance the photocurrent response and hence charge separation efficiency.

Ternary construction of Z-scheme $\text{g-C}_3\text{N}_4/\text{ZnO}@\text{Fe}_2\text{O}_3$ synthesized by direct pyrolysis followed by sol-gel method photodegraded of 99.3% tartrazine in 35 min under visible light [84]. The band gap value for $\text{g-C}_3\text{N}_4$, ZnO , $\text{ZnO}@\text{Fe}_2\text{O}_3$ and $\text{g-C}_3\text{N}_4/\text{ZnO}@\text{Fe}_2\text{O}_3$ were 2.7, 3.1, 2.5 and 2.6 eV, respectively (Figure 7e). The rate of recombination and charge carrier separation were studied by PL spectroscopy. The lower PL emission peak represents lower recombination rate in heterojunction as compared to bare photocatalysts (Figure 7f). The Z-scheme based photocatalyst exhibit higher charge migration for degradation of organic pollutants than conventional type-II heterojunction photocatalyst.

Figure 7: (a) Charge migration of ZnS/Fe₂O₃ [80] (b) charge trapping experiment [82] (c) Double Z-scheme of Fe₂O₃@NiFe₂O₃P-g-C₃N₄ [83] (d) LSV plots of Fe₂O₃@NiFe₂O₃P-g-C₃N₄, Fe₃O₄ and NiFe₂O₃P-g-C₃N₄ [83] (e) PL spectra of g-C₃N₄/ZnO@α-Fe₂O₃ [84] (f) optical band-gap of g-C₃N₄, ZnO, ZnO@α-Fe₂O₃ and g-C₃N₄/ZnO@α-Fe₂O₃ nanocomposite [84].

4.4 S-scheme based ferrite heterojunction

The S-scheme heterojunction were constructed by combining reduction and oxidation photocatalysts having staggered type band structure similar to type-II heterojunction. The reduction photocatalysts generally used for solar fuel generation where VB holes are futile and needs to be removed by sacrificial agent. Whereas, oxidation photocatalysts were greatly utilized in photodegradation in which CB electrons are useless. Though, the arrangement of two semiconductor the S-scheme is similar to type-II heterojunction but differ in charge migration pathway. Here, the electron diffuses at the interface from semiconductor with lower to higher work function and continue till the Fermi level of two semiconductor get equilibrated [85]. The electron diffusion creates internal electric field at the interface and alignment in Fermi level that exhibit upward and downward band bending at SC 1 and SC 2, respectively (Figure 8a). Band bending and internal electric field demonstrated driving force to proceed recombination of useless electron if SC 2 and holes of SC 1. However, electrons and holes with high redox potential were

persisted in CB of SC 1 and VB of SC 2, respectively beneficial for spatial charge separation. S-scheme charge migration mechanisms resemble 'step' (low CB to high CB) as in macroscopic system.

Further, such type of charge migration can be established by various characterization technique such as XPS, ESR, AFM, M-S plot and PL. As after charge migration the semiconductor surface display increase or decrease in electron density after contact which alters the effective nuclear charge and hence the binding energy of element. In S-scheme heterojunction effective electron-hole movement and separation is possible due to effective interfacial contact between reduction and oxidation semiconductor [86]. The close contact between semiconductors can be analysed by AFM technique. Figure 8b, c microscale thickness of WO_3 (3.0nm) and g- C_3N_4 (2.5nm) showing strong electrostatic interfacial contact in $\text{WO}_3/\text{g-C}_3\text{N}_4$ assist in facile charge migration. Due thin layered structure of heterojunction formation the strong columbic force increases the internal electric field. The work function as calculated by DFT for WO_3 (6.23eV) is larger than g- C_3N_4 (4.18eV) semiconductor (Figure 8d and e). Noticeably, g- C_3N_4 shows upward band-banding with strong reduction potential by releasing $\cdot\text{O}_2^-$ and WO_3 exhibit downward banding with involving $\cdot\text{OH}$ radical. This support the S-type charge migration pathway in $\text{WO}_3/\text{g-C}_3\text{N}_4$ heterojunction.

Figure 8: (a) S-scheme based mechanism [85] AFM images of (b, c) [86] WO_3 nanosheets and (d, e) g- C_3N_4 nanosheets [86].

In the other context, M-S plot characterized S-scheme in which TiO_2 (3.2eV) having larger band-gap than PDA (1.6 eV) having high LUMO of PDA then CBM of TiO_2 (Figure 9a) [87]. The electron migrated from PA to TiO_2 unless Fermi level equilibrates and Fermi level of TP_3 nanocomposite shift upward compare to TiO_2 . It examined that coupling of more negative band potential in TP_3 with PDA can increase reduction potential of TiO_2 . Therefore, high charge density of TP_3 was efficient for enhancing the charge separation. S-scheme also characterized by electron EPR spectra in which DMPO- $\cdot\text{OH}$ signal observed for PDA due to negligible oxidation potential of holes and strong signal in T and TP_3 because holes exist in VB of TiO_2 (Figure 9b). Further, in DMPO- $\cdot\text{O}_2^-$ signal of PDA due to photo-excited electron in LUMO were recombine with holes in HOMO owing to narrow band gap (Figure 9c). Thereafter, DMPO- $\cdot\text{O}_2^-$ peaks of T and TP_3 exhibit reduction capability and reduces O_2 to $\cdot\text{O}_2^-$. According to this photo-excited holes exist in VB of TiO_2 so by the charge migration mechanism they explained S-scheme.

For instance, non-toxic S-scheme based $\text{SnFe}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$ heterojunction prepared by optimizing SnFe_2O_4 content to 5% via solvothermal method [88]. The heterojunction photo-catalytically degraded 93% of tetracycline whereas, COD decrease to 77%. The direction of charge migration in S-scheme heterojunction is kinetically and thermodynamically favourable. Transient photocurrent and EIS measurement analysed separation and movement of charge carrier around heterojunction. As clearly observe in Figure 9d the large arc radius exhibits lower separation and migration efficiency thus excessive addition of SnFe_2O_4 enhance the recombination rate of electron-hole pair in $\text{SnFe}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$. SnFe_2O_4 content increases 5% of composite exhibiting smallest arc radius with fast separation and migration of charges so it leads to increase in charge transfer resistance. The electron migration pathway in $\text{SnFe}_2\text{O}_4/\text{ZnFe}_2\text{O}_4$ heterojunction follow S-scheme. Here, due to formation internal electric field electron in the CB of ZnFe_2O_4 recombine with VB holes of SnFe_2O_4 . As the VB edge potential of both SnFe_2O_4 and ZnFe_2O_4 is 1.54 and 1.55 eV, respectively which is not sufficient for $\cdot\text{OH}$ generation thus remaining holes in the VB of SnFe_2O_4 participates in degradation process. While, electron in the CB of SnFe_2O_4 successfully reduces O_2 molecule to $\cdot\text{O}_2^-$ radical. The trapping experiment also support the $\cdot\text{O}_2^-$ radical and holes as active species in degradation.

Another step-scheme $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ heterojunction was utilized as adsorbent and photocatalyst for the removal of U(VI) [89]. Nearly 94% and 1892mg/g of U(VI) is adsorbed and photo-catalytically reduced from pH=5-6. The property of adsorbent influenced by pore volume and large specific surface area that give more active sites for adsorption of pollutant. Also, pH of the solution greatly influence the ionic state of

uranium, and surface charge on adsorbent. At low pH 3 to 4 uranium exist as UO_2^{2+} and the surface of $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ is also positively charged. This greatly reduces the adsorption capacity due to the repulsive forces between the adsorbate and adsorbent as well as the competitive adsorption between UO_2^{2+} and H^+ . As the pH increases positive charge of uranium decreases and the surface of heterojunction also become negatively charge. Thus, repulsive forces changes to attractive forces at higher pH which significantly enhance the removal efficiency at pH 5-6. XPS spectra of $\text{ZnFe}_2\text{O}_4/\text{g-C}_3\text{N}_4$ is obtained after adsorption and photoreduction of U(VI) (Figure 9e).

The two peak appeared at 392.26 and 381.75 eV ascribed for U $4f_{5/2}$ and U $4f_{7/2}$ indicative of U (VI) absorption on the heterostructure surface. Subsequently, two peaks at 390.66 and 379.95 eV were assigned for U $4f_{5/2}$ and U $4f_{7/2}$ of U(IV) after photoreduction of U(VI) into U (IV). Further, to reveals the adsorptional mechanism adsorption kinetics were studied. The adsorption mechanism obeys pseudo second order kinetics as higher correlation coefficient ($R^2=0.996$) were obtained in comparison to pseudo first order kinetics ($R^2=0.969$). Also, the calculated adsorption capacity ($q_e=219$ mg/g) is near to the experimental value ($q_e=189$ mg/g) when applied pseudo second order model. The kinetic study reveals that chemisorption step is the rate determining step. Further, Langmuir has prominent coefficient ($R_2=0.993$) than Freundlich ($R_2=0.933$) that demonstrating monolayer adsorption. The S-scheme type electron migration were also supported by DFT calculation, the work function of $\text{g-C}_3\text{N}_4$ (4.63eV) higher than that of ZnFe_2O_4 (3.95eV). Therefore, initially electron diffuses from ZnFe_2O_4 to $\text{g-C}_3\text{N}_4$ until their Fermi level equilibrated and generates built-in electric filed. The built-in electric filed assist in recombining the CB electron of $\text{g-C}_3\text{N}_4$ with the VB holes of ZnFe_2O_4 . Such type of electron migration pathway renders the electron and holes with strong reducing and oxidizing ability.

The ternary $\text{rGO/g-C}_3\text{N}_4/\text{CoFe}_2\text{O}_4$ heterojunction fabricated by hydrothermal method obeying S-scheme type charge migration pathway degraded 97% of nitrophenol under visible light [90]. The increasing degradation efficiency shows high surface area, effective charge separation and mobility of nanocomposite. The 2D rGO nano-sheet contains sp^2 hybridized carbon atom that provide fast charge carrier mobility and large active surface area. The photoexcited CB electron of CoFe_2O_4 transferred to VB of $\text{g-C}_3\text{N}_4$ via rGO surface (Figure 9f). The CB of $\text{g-C}_3\text{N}_4$ has negative potential compared with standard reduction potential (-0.33V), that can reduces O_2 to $\cdot\text{O}_2^-$ radical. The magnetic nature of ternary heterojunction was examined by VSM hysteresis loop. The heterojunction exhibits ferromagnetic property at room temperature displaying magnetic saturation of 15.58emu/g for bare CoFe_2O_4 and 11.49 emu/g for ternary heterojunction. Combining non-magnetic rGO and $\text{g-C}_3\text{N}_4$ reduces the magnetic saturation of ternary

heterojunction. From the reported literature it can be concluded that S-scheme type charge migration is intrinsically more feasible over type -II and Z- Scheme. The effective charge carrier separation, recombination of useless electron-holes pair and utilization of high oxidation and reduction potential makes S-scheme more adaptable. Lastly, we have summarizes various ferrite based heterojunction obeying type-II, Z-scheme and S-scheme pathway for the pollutant photodegradation are listed in Table 1.

Figure 9: (a) Mott-Schottky plots of T and TP3 (b) EPR spectra of DMPO-•OH (c) in aqueous and DMPO-•O₂⁻ in methanol dispersion in the presence of T, TP3 and PDA [87] (d) XPS of ZnFe₂O₄/g-C₃N₄ [89] (f) Charge migration mechanism of r-GO/g-CN/CF0 [90].

Table1: Summary of ferrites-based nanocomposite for the pollutant photodegradation.

Ferrite based photocatalyst	Synthetic method	Pollutant	Photocatalytic Condition	Photocatalytic Performance	Type of charge migration	Reactive oxygen species	Recyclability	Ref.
ZnFe ₂ O ₄	Reduction-oxidation method	Orange II	Light flux zone of Xe lamp. Vis- ≥ 420 nm pH = 3.0~9.0	78.6% of Orange II degradation	NA	SO ₄ ²⁻ , ·OH	5 cycle	[71]
Fe ₂ TiO ₄	Laser ablation approach	Rhodamine	150 W visible light lamp 485nm	80% of RhB degradation	NA	e ⁻ , h ⁺	2 cycle	[91]
Ni-ZnFe ₂ O ₄	Sol-gel method	Rhodamine	Conc. of Ni-ZnFe ₂ O ₄ =0.5g Conc. of RhB=250 ml of 10 mg/l Light flux zone of Xe lamp 552 nm	98% of RhB degradation	NA	·OH, ·O ₂ ⁻ , and h ⁺	5 cycle	[92]
Co _{1-x} Zn _x Fe ₂ O ₄	Microwave combustion method	Rhodamine	Conc. of dye - 6mg/l 150 W Halide lamp UV-330 nm pH 2.0	99.9% of RhB degradation	NA	·OH	5 cycle	[73]
Au-Zn _x Fe ₂ O ₄	Thermal evaporation	Rhodamine	Conc. of dye = 5µm of 10ml 150-W xenon lamp Vis - 554 nm	31% of RhB degradation	NA	·OH, ·O ₂ ⁻ , and h ⁺	3 cycle	[93]
TiO ₂ -ZnFe ₂ O ₄	Citrate gel auto combustion method	Methyl-red and thymol blue	450 W Xe arc lamp 350 to 550 nm	90 % Methyl-red and thymol blue of degradation	Type-II	e ⁻ and h ⁺	4 cycle	[94]
CoFe ₂ O ₄ -PANI	Hydrothermal method	Methyl Orange and Methyl blue	> 420 nm 500 W Hg and Xe lamp,		Type-II	·OH	3 cycle	[95]
NiFe ₂ O ₄ /Bi ₂ O ₃	Hydrothermal	Tetracycline degradation	Conc.=100 ml of 10 mg/L	90% of TC degradation	Type-II	h ⁺	3 cycle	[74]

	method		150W xenon lamp 420nm						
TiO ₂ @CuFe 2O ₄	Sol-gel method	2,4- dichlorophen oxyacetic acid (2,4- DP)	Conc.= 10 to 60 mg/L, low 6W pressure mercury UV-C lamp (λ = 254 nm pH = 6.5 $\pm$ 0.2	97.2% of 2,4- DP degradation	Type-II	SO ₄ ²⁻ , ·OH, ·O ₂ ⁻	5 cycle	[60]	
ZnFe ₂ O ₄ – TiO ₂	Solvother mal method	Bisphenol A degradation	Conc.= 10 mg L ⁻¹ 10 W LED lamp 465 nm pH 7	>99% of BPA degradation	Type-II	h ⁺ , ·OH	10 cycle	[96]	
POPD- CoFe ₂ O ₄	Microwav e-assisted	Tetracycline	Conc. 100 mL, 20 mg/L XE300, power 300 W, 380 nm -780 nm	45.98 % of TC degradation	Type-II	e ⁻ and h ⁺	5 cycle	[97]	
ZnF ₂ O ₄ /g- C ₃ N ₄	Polymeriz ation method	Ciprofloxac in degradation	$\lambda \geq 400$ nm	92% of CIP degradation	Type-II	e ⁻ , h ⁺ ·OH and ·O ₂ ⁻	4 cycle	[98]	
ZnS/Fe ₂ O ₃ /r GO	Hydrother mal method	Methylene blue	150 μ l of TGA Xe lamp 300 W with a 420 nm	96.45% of MB degradation	Z-scheme	·OH, ·O ₂ ⁻ and h ⁺	5 cycle	[80]	
Bi ₂ Fe ₄ O ₉ /Bi ₂ WO ₆	Hydrother mal method	Rhodamine	10 mg L-1 of RhB 300 W xenon lamp (>420 nm	100% of RhB degradation	Z- scheme	·OH, ·O ₂ ⁻ , and h ⁺	5 cycle	[99]	
Bi ₁₂ O ₁₇ Cl ₂ /A g/AgFeO ₂	In-situ deposition - precipitati on method	Tetracycline	0.5 g L ⁻¹ 3.3 < pH < 7.68)	87.4% of TC degradation	Z-scheme	·O ₂ ⁻	6 cycle	[62]	
ZnO/NZF	Precipitati on method	Rhodamine	30 mL of RhB A 250W high- pressure Hg lamp 500W	94% of RhB degradation	Z- scheme	·O ₂ ⁻	NA	[102]	

			Xenon lamp >420 nm						
NiFe ₂ O ₄ /BiPO ₄	Hydrothermal method	Tetracycline and Rhodamine B	50 mL of TC	TC (98%) and RhB (99%) of degradation	Z-scheme	·OH, ·O ₂ ⁻ , and h ⁺	4 cycle	[82]	
ZnFe ₂ O ₄ /NC Ds/Ag ₂ CO ₃	Hydrothermal and calcined method	Levofloxacin	Conc. of LFLX =0.60 g/L Conc. of ZnFe ₂ O ₄ /NCDs/Ag ₂ CO ₃ =10 mg/L 300 W Xe lamp 420-760nm	88.75% of LFLX degradation	Z-scheme	·OH ·O ₂ ⁻ and h ⁺ ,	5 cycle	[100]	
Fe ₃ O ₄ @NiFe ₂ O ₄ /P-g-C ₃ N ₄	Sol-gel method	Ciprofloxacin	Conc. of CIP =20 mg L ⁻¹ Xe lamp with an excitation wavelength of 330 nm.	90% CIP degradation	Z-scheme	·OH, ·O ₂ ⁻ , h ⁺ , and e ⁻	4 cycle	[83]	
PANI/AgFeO ₂	In situ growth	Tetracycline	20 mg L ⁻¹ of TC 300 W xenon lamp below 420 nm (3.3 < pH < 7.68	91.8% of TC degradation	Z-scheme	h ⁺ , ·OH and ·O ₂ ⁻	4 cycle	[101]	
g-C ₃ N ₄ /CoFe ₂ O ₄	Hydrothermal method	4-Nitrophenol	Conc. of 4-NP=20 mg/l pH=7	97% of 4-NP degradation	S-scheme	OH·	4 cycle	[90]	
SnFe ₂ O ₄ /ZnFe ₂ O ₄	Solvothermal method	Tetracycline	Conc. of TC=100 mL of 10 mg/L 300W xenon lamp 400 nm pH = 11	93.2% of TC degradation	S-scheme	h ⁺ ·OH and ·O ₂ ⁻	4 cycle	[88]	
ZnFe ₂ O ₄ /g-C ₃ N ₄	Hummers' method	Hexavalent uranium	Conc. of (U(VI)) =699.3 mg/g 8 W LED pH 5.0	90% of (U(VI)) degradation	S-scheme	e ⁻ , h ⁺ ·OH and ·O ₂ ⁻	5 cycle	[89]	

Conclusion and Outlook

In this manuscript, efforts have been put to explore the recent development of ferrites based nanocomposites explored for photocatalytic wastewater treatment. The basic

information on the structural and properties with various synthetic methods of ferrites with versatile morphology, phases, crystalline structure and dimensionality were discussed so as to provide depth insight on ferrites nanocomposites. The influence on the morphology, properties and activity of ferrites nanoparticles by altering the synthetic approaches were discussed. The ferrites exhibit excellent superparamagnetic properties beneficial for its utilization in various photocatalytic processes, facile separation and improved reusability. Furthermore, there are several studies reported the usage of bare ferrites photocatalyst and modified ferrites that dispenses several advantages in photodegradation processes. Still there are few practical issues in the utilization of ferrites nanoparticles in large scale which further needs to be explored. The ferrites-based nanocomposite should be prepared without liberating its magnetic properties. Under different reaction conditions ferrites can undergo phase transformation which changes their microstructure properties, magnetic behavior and may introduce defects. Investigation in the field of metal defects and generation of oxygen vacancies in ferrites surface are still meagre. These defects have ability to alter the band structure of materials and traps the electrons that can enhance photoactivity of materials.

The ferrites can be modified by constructing heterojunction working via either type-II, Z-scheme or S-scheme mechanism. Fabrication of heterojunction were considered more effective due to the combination of synergistic effect of individual photocatalysts rather than doping or introducing defects. During heterojunction formation the semiconductor with appropriate band edge potential must be carefully chosen in such as way so as to impart higher photoefficiency. The ideal heterojunction should have high surface area, large no of active site, highly chemically and thermally stable, cost-effective, environmental friendly, good uniform dispersion of NPs, broad absorption range, facile charge migration, low rate of recombination, generation of both hydroxyl and superoxide radical, multi-dimension electron migration pathway, high porosity etc. In the near future, we believe outstanding ferrite based photocatalyst with superior photoefficiency may be fabricated and explored for various applications.

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