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PHOTOCATALYTIC ACTIVITY OF SOME SPINEL FERRITE NANOCRYSTALS

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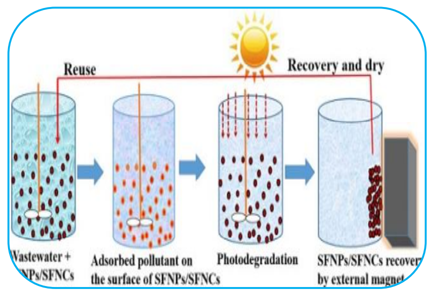
ABSTRACT:

This review focuses more on the novel aspects of recent developments in the photocatalytic application of spinel ferrite nanoparticles and their nanocomposites to wastewater pollutant degradation capacities. Spinel ferrite nanoparticles used as a photocatalyst in wastewater treatment's potential recovery and reuse are also discussed. An overview of the cutting-edge methods that are required to modify the surface of spinel ferrite nanoparticles, nanocomposites, and their selectivity for the degradation of various pollutants is provided. Finally, in order to enhance the photocatalytic application of spinel ferrite nanoparticles and their nanocomposites, issues, gaps, and needs for future research are discussed. Spinel ferrite nanoparticles are metal oxides with a spinel structure that have the general formula AB2O4, where A and B represent various metal cations that are at least tetrahedral or octahedral with ferric in the chemical formula. Spinel ferrite nanoparticles are also known as spinel ferrite. At both locations, the metal cations are coordinated to oxygen atoms by tetrahedral and octahedral means, respectively. The types, amounts, and positions of the metal cations in the crystallographic structure of ferrites have a significant impact on their physicochemical properties; a typical structure for spinel ferrite is depicted in. Ferrites are used in a wide range of industries and biomedical applications.



KEYWORDS: *Organic pollutant, Spinel ferrite nanocomposite, Photocatalyst, Photodegradation of Wastewater, and Spinel ferrite nanoparticle.*

INTRODUCTION

In the first scenario, SFNPs are most commonly used for cancer diagnosis, cancer gene therapy, and drug delivery. In the second scenario, SFNPs can be used as a catalyst, remove pollutants through adsorption or photodegradation as a gas sensor in a high-frequency device for water splitting, and modify membranes. When SFNPs are used as a catalyst, they help speed up the rate of chemical reactions in a variety of organic and inorganic synthesis processes, as well as Using an external magnetic field, SFNPs can be easily separated from the solution mixture after treatment is finished. These SFNPs are especially important for increasing reaction yield, lowering the required reaction temperature, and promoting particular chemical reactions. Their nanoparticles and nanocomposites are used for wastewater treatment, and their photodegradation capacity for organic pollutants is another important feature. Numerous studies have demonstrated that SFNPs-based catalysts are extremely useful for the complete removal of contaminants due to their strong photodegradation capabilities. The formation of more toxic byproducts than the parent pollutants may result from incomplete removal or degradation of pollutants. Therefore, it is inevitable to look for nanoparticles (NPs) and nanocomposites (NCs) with strong photodegradation capacities in order to reduce this incidence. Simultaneously, SFNPs could be utilized as antibacterial specialists during wastewater treatment. In particular, the antibacterial properties of commonly used SFNPs are enhanced when transition metals are partially substituted. Recent research has also shown that zinc substituted cobalt ferrite is more effective than Mn(II) and Cu(II) substituted cobalt ferrite against drug-resistant bacteria. In addition to their use in the biological and industrial sectors, this additional advantage of SFNPs may open up a fascinating research field.

Commonly used spinel ferrites

Fe_3O_4, $CoFe_2O_4$, $CuFe_2O_4$, $MnFe_2O_4$, $NiFe_2O_4$, and $ZnFe_2O_4$ are the most common SFNPs and their derivative composites that could be utilized as a photocatalyst. These SFNPs could be attached to a common photocatalyst to give it magnetic properties, make it easier to separate from an external magnetic field, and improve stability and photocatalytic degradation of contaminants. The photocatalyst degradation capacity of bare Fe_3O_4 NPs towards inorganic and organic pollutants is poor in comparison to its composites such as Fe_3O_4, TiO_2 or Fe_3O_4, TiO_2, SiO_2. For instance, about 98.7 and 91.5% photodegradation of ampicillin over Fe_3O_4, TiO_2/Ag NCs was achieved under UV and visible light irradiation after 6 h, respectively. When only bare Fe_3O_4 microspheres of an average size of 350 nm were used, only about 30% of ampicillin was photodegraded.

Numerous researchers have also noted that the $CoFe_2O_4$ and $CuFe_2O_4$ NPs and their corresponding NCs have the best catalytic properties. It has been demonstrated that both NPs and NCs have photocatalytic capabilities for wastewater treatment. For instance, the photocatalytic activity of $CoFe_2O_4$, ZnS was found to be significantly higher than that of bare $CoFe_2O4$ NPs and ZnS when wastewater containing methylene blue (MB) was subjected to ultrasound irradiation. $CoFe_2O_4$, GO was also found to have a greater effect on MB photodegradation than pure $CoFe_2O_4$ and GO alone. The improved adsorption capacity, ease of electron transfer from $CoFe_2O_4$ NPs to graphene sheet, and restriction of electron recombination are primarily responsible for the enhanced photodegradation. Additionally, the core-shell nanostructures of cobalt ferrite make it possible to recover and reuse the nanocomposite multiple times and contribute to its value as a cost-effective treatment.

Photocatalytic application of SFNPs and SFNCs for wastewater remediation

Worldwide concern stems from the presence of various contaminants in industrial wastewater discharges. Treatment and removal of toxic organic contaminants like dyes, phenols, chlorophenols, and nitro-phenols have been difficult for a very long time, especially when exposed to visible light. In wastewater treatment technology, metal oxides and semiconductors have gained a significant amount of attention for their photocatalytic degradation capacity of pollutants. Numerous studies have demonstrated the possibility of removing these contaminants by a photocatalytic approach using SFNPs, and this is the primary focus area of recent research. It has been reported that SFNPs and their NCs possess both of the aforementioned properties, making them suitable for use as photocatalysts in wastewater treatment. The application of SFNCs for wastewater treatment as either an adsorbent or a photocatalyst is one of the most intensively researched areas at the moment and may be one of the most cost-effective methods. SFNPs easily convert visible light energy into chemical energy to support oxidation and reduction due to their low energy band gaps. Preferably, wastewater containing natural toxins can be treated by photocatalytic materials and the natural poisons can be corrupted into CO_2(g), H_2O(l) and other vaporous synthetics relying on the basic sythesis of the natural contaminations, without the development of waste. As a result, in the presence of oxidants like H_2O_2, photocatalytic degradation and removal of organic contaminants are regarded as environmentally friendly, straightforward, and effective methods. In fact, when combined with other light-sensitive strong oxidants and semiconductors, their high photodegradation capacity for pollutants is significantly enhanced. In this section, the mechanism of contaminant degradation caused by photocatalyst effects of SFNPs or their corresponding composites, as well as the advantages of incorporating SFNPs into semiconductors, particularly the reduction of corrosion, band gap, and electron-hole recombination, are briefly discussed.

Mechanism of contaminant degradation

Within the sight of SFNPs-semiconductors, photodegradation of natural pollutants could be effectively plausible. Because, provided that the light energy is greater than the energy band gaps of photocatalytic materials, an electron is excited from the valence band to the conduction band of the photocatalyst, leaving behind a photo-generated hole, when contaminated water is exposed to light energy in the presence of SFNPs-semiconductors. The delivered e-is handily caught by broken down oxygen gas accessible in the water at the conduction band The receptive oxygen free revolutionary further responds with hydrogen particle to frame a functioning free hydroxyl revolutionary and hydroxyl particle responds with water to yield dynamic hydroxyl free revolutionaries . The contaminants are at a close proximity to the active radicals because of the high adsorption capacity of SFNPs. They are then quickly and easily degraded by the hydroxyl radicals that are produced on the surface of the photocatalyst. This is followed by the desorption of the degraded products from the ferrite active surface sites. Direct reduction by electrons in the conduction band and oxidation by holes in the valence band are two possible pathways by which organic pollutants can be degraded. The schematic diagram for the formation of reactive oxygen and hydroxyl radicals is shown in Figure. 3. Ferrites can use visible light because of their low energy band gap. As a result, they are highly desired for their ability to break down pollutants in wastewater and water. Table 1 contains a list of selected ferrites and semiconductors along with their band gap energies. Table 1 reveals that ferrites have a lower energy band gap than semiconductors, making them suitable for visible light absorption. In this way, NCs arranged by fuse with SFNPs enjoy a few benefits, for example, diminished energy band hole that can use noticeable light, further developed dependability, simplicity of division from the response combination by an outside attractive field, and a few times conceivable reusability

Dye degradation

Organic compounds called dyes are used to color things like clothing and textiles. When they are dissolved in an aqueous medium, their particle charge is usually used to classify them. They were mostly divided into natural and synthetic dyes, which were further divided into anionic, cationic, and non-ionic dyes based on the charges they carried when they were ionized. The majority of dyes are stable and difficult to break down due to their complex structures, which make them unique. If dyes get into water resources, they can easily pollute the entire system and have devastating effects on everyone's health. The release of toxic chemicals through slow degradation through oxidation, hydrolysis, physical interaction, and chemical reactions has been the primary cause of dyes' toxic effects on aquatic life, even at low concentrations. Additionally, dyes severely harm aquatic life by preventing light from entering the water system and reducing the photosynthetic reaction. In addition, the cancer- and mutagenic effects of dyes make them toxic to humans, animals, and aquatic life.

Therefore, dye removal from water and wastewater is one of the environmental priorities from a health and environmental perspective in order to adequately safeguard human health and the health of other organisms that rely on water. However, dyes' resistance to chemical and biological degradation makes it difficult to treat contaminated water. As of late, SFNPs and their NCs have been perceived areas of strength for having properties towards color debasement in the apparent light Phenol and phenol subsidiaries are among the serious biggest gatherings of ecological toxins. This is primarily because they are widely used in industry as antibacterial and antifungal agents. Due to their toxicity, carcinogenicity, and mutagenic nature, these compounds are considered priority organic pollutants by the US Environmental Protection Agency. Even at very low concentrations, they can severely harm human and animal liver, lung, and red blood cells. Additionally, the stability of these pollutants makes degradation challenging. Thusly, they stay in the climate for longer periods .In the resulting segments, conceivable photodegradation of phenol and its most generally utilized subsidiaries, for example, chloro-and nitro-phenol are momentarily explored.

Phenol

Phenol is one of the most prevalent chemicals in wastewater and one of the pollutants with high toxicity and low biodegradability. Even at low concentrations, it could harm human health severely. Photocatalytic use of SFNPs to completely degrade and remove phenol from wastewater is becoming increasingly common in recent years. For instance, in wastewater containing phenol, application of Fe3O4 mixed with H2O2 removed 85 percent of the phenol in three hours at a temperature of 16 degrees Celsius without the formation of any secondary pollutants. The photocatalytic degradation of phenol using Fe3O4ZnO hybrid NPs has recently been investigated, and incorporating semiconductors into ferrite also increases the rate of phenol degradation. The hybrid NPs' stability and recoverability were also evaluated during the study. After three cycles, 89% of the used photocatalyst was recovered, with phenol removal rates of 82.8, 72.4, and 65.1 percent in cycles one, two, and three, respectively. These values are much higher than those of freshly prepared ZnO, where only 52% of phenol was broken down. This suggests that synthesised hybrid photocatalysts have better photo-catalytic activities, are more stable, and are easier to recover. The synergistic effects between SFNPs and semiconductors could be responsible for the improved photocatalytic performance. These effects reduced the rapid recombination of photogenerated electrons and holes, which improved the efficiency of charge separation and made more electrons and holes available for the reduction and oxidation of contaminants.

Nitrophenol

The removal of nitrophenol from wastewater either through degradation or conversion into their corresponding useful amino-aromatic components is extremely necessary due to the carcinogenic nature of organic nitro compounds, which are among the non-biodegradable organic pollutants and commonly found in wastewater discharged from industries and agricultural wastes. Actually, converting nitro-phenol into useful amino-aromatics has more advantages because amino-aromatics are one of the most important organic compounds for the synthesis of several industrial dyes, pharmaceuticals, photographic developers, corrosion inhibitors, and biologically active compounds. Photo-reduction, heterogeneous catalytic hydrogenation, and other methods can be used to convert nitro-phenol into useful amino-aromatics. However, the use of pure or substituted SFNPs for the reduction of nitro-phenol could eliminate all of these limitations, including the difficulty of catalyst recovery, the need for energy, and the length of time required. MnFe2O4 NPs, for instance, have shown high catalytic performances in the reduction of 4-nitrophenol, 2, 4, 6 tri-nitro-phenol, and 4-nitroaniline with 100% conversion into their corresponding amino derivatives in 4.5 min reaction time, out of three distinct spinel ferrites synthesized using sol-gel hydrothermal technology.

Antibiotics

The misuse or overuse of antibiotics by humans may increase the development of antibiotic-resistant bacteria and contribute to the spread of various antibiotics into aquatic ecosystems. Even when antibiotics are used as usual to treat infections, they are hard to break down, so antibiotic residues are released into the environment through feces and urine. Antibiotics may become more resistant to bacteria as a result of their release into the environment, which could have a significant impact on their efficacy. Additionally, conventional water treatment methods barely remove these antibiotics. Through photocatalytic treatment, antibiotic degradation from water and wastewater has received more attention in recent years. It is regarded as one of the most promising photocatalysts for the breakdown of antibiotics. The photocatalytic performance of pyrrole imprinted NCs for the degradation of 2-mercaptobenzothiazole was evaluated in another study. The outcome demonstrates the photocatalyst's dual functions, which include strong ability to selectively recognize and photodegrade 2-mercaptobenzothiazole and high photocatalytic efficiency. In general, these results indicate that SFNC photocatalysts hold promise for efficient antibiotic degradation.

Photo-corrosion reduction

All semiconductors with the right energy band gaps, according to a number of studies, are not suitable for photocatalytic wastewater treatment. This is because some semiconductors are photoinstable, so photocorrosion of semiconductors takes precedence over water oxidation. For instance, in fluid arrangement, show photograph shakiness when illuminated with UV light and go through photograph erosion. What's more, unfortunate usage of apparent light and high recombination paces of charge transporters are the principal issues with unadulterated .It ought to be noticed that 90% of photograph produced electron-opening matches recombine in under 10 nano-seconds and thusly photograph created charge transporters accessible for surface responses will be restricted. In the employed condition, 80% of RhB was degraded during the first cycle of pure application; incorporating a small amount of SFNPs improves photo-stability of these semiconductors. However, only 30% of RhB was degraded during the third cycle, indicating a significant decrease in photocatalytic activity. effect on photocatalytic activities after three cycles The schematic diagram of the two NCs exposed to visible light is depicted in Figure. 6b. The result clearly demonstrates the significance of incorporating SFNPs into CdS, which increased charge separation efficiency and reduced photocorrosion by reducing the rate of electron-hole pair recombination probability, resulting in high stability and photocatalytic performance. For hybrid, similar outcomes have been reported. It should be noted that UV light contributes 4 and visible light contributes 43% of the total energy of the sun on Earth, respectively. Along these lines, alteration of semiconductors with huge band hole, for example, are vital to cause them to use high level of free apparent light energy for photocatalytic enactment. For instance, the energy band gap of has been reduced to as a result of surface doping, enhancing its photocatalytic activities and increasing its capacity to harvest visible light. In a similar vein, multi-porous nanotubes produced by combining simple electrospinning with calcination processes have demonstrated high photocatalytic stability.

Improving catalytic efficiency and selectivity of SFNPs

For effective photocatalytic execution, fundamental, the NPs or NCs material priority great security and adsorption limit of fluid stage toxins . When SFNPs are used for catalytic photodegradation or the selective removal of contaminants through adsorption, there are a number of ways to increase their selectivity and catalytic efficiency. Surface immobilization with metals/semiconductors, elemental doping, and the creation of binary or tertiary hetero-junctions with a variety of photoactive materials, such as those that boost catalytic efficiency, are just a few examples. While the selective removal of contaminants is aided by the functionalization of photocatalytic materials with particular organic moieties that have a high capacity for adsorption of the targeted contaminants. It is anticipated that the enhanced photocatalytic activity of the modified SFNPs will allow them to withstand the oxidative and reducing effects of chemicals when exposed to light in the majority of instances. In addition, the surface modification may aid in the stabilization of SFNPs by enhancing hydrophobic interactions or end-grafting, encapsulation, or improving water dispersibility.

In a similar vein, the photocatalytic activity of SFNPs can be enhanced by either reducing the energy band gap or enhancing the crystalline characteristics by doping ferrite with representative, transition, or rare earth metal ions of a small size. Sol-gel synthesis of stable and crystalline Ru-doped SFNPs like $NiRu_{0.4}Fe_{1.6}O_4$ and $CuRu_{0.1}Fe_{1.9}O_4$ was used to photodegrade remazol deep red dye and the antibiotic ciprofloxacin completely within 5 and 90 minutes, respectively. R-doped SFNPs had higher photocatalytic activities than un-doped ones. In a similar vein, the photodegradation of malachite green was enhanced in comparison to that of the undoped NPs when a trace amount of aluminum was added to six distinct SFNPs. Each Al-doped SFNP had an extremely high capacity for photodegradation. The increased crystallinity and ease of ion mobility may be related to the improved photocatalytic properties obtained with a small amount of Al doping. The substituted dopant will result in crystal defects in the crystal lattice due to the different ionic sizes of the dopant and parent metal ions. As a result, the different photodegradation activities of SFNPs are attributed to the differences in electron concentration and active site on the doped surface and the variation in crystal defects in the structure. The effects of surface immobilization, functionalization of photocatalysts, and doping of rare earth metals are briefly discussed in the following sections.

Surface immobilisation with metal or semiconductors

The incorporation of SFNPs enhances the efficiency and recoverability of photocatalytic materials. In point of fact, surface immobilization of photocatalysts is thought to reduce their surface area, which in turn reduces their photocatalytic activity. However, combining or doping SFNPs with semiconductors with a high energy band gap helps to reduce the energy band gap between UV and visible light ranges, enhances their photocatalytic activity, and increases their recoverability from an external magnetic field. In addition, surface immobilization of SFNPs with metals, semiconductors, or organometallics increases photocatalytic activities, decreases the likelihood of e- and h+ recombination, and improves the NPs' stability in basic and acidic conditions. For example, aerobic oxidation and the conversion of a number of primary and secondary benzyl alcohols into carbonyl compounds were successfully accomplished with the help of a photocatalyst made from phosphor-tungstic acid, supported on imidazole-functionalized silica, and coated with cobalt ferrite nanoparticles. In a similar vein, when exposed to ultraviolet light, the NPs produced using the Sol-gel method demonstrated a high capacity for photodegradation of the MB dye found in contaminated water. This study demonstrated that organic dyes could be removed by 98.5 percent in just 40 minutes. In addition, the amount of photocatalytic loading, the initial dye concentration, and the pH of the wastewater all had an impact on the organic dyes' degradation efficiency, as did other studies.

Increasing surface area and crystallinity

Contaminants can be easily absorbed by photocatalytic materials with crystalline morphologies and a large surface area. A high adsorption capacity of pollutants by good photocatalytic NPs or NCs is one of the essential prerequisites for effective pollutant degradation in wastewater treatment. Because active radicals generated by photocatalytic materials during the reaction can easily attack and degrade pollutants that are in close proximity to photocatalytic materials. Similarly, crystalline NPs improve photocatalytic activity and facilitate charge transport. High-temperature treatment can yield NPs with good crystallinity, but this may result in an increase in particle size. As a result, it is necessary to devise every strategy for increasing the surface area of the particles while maintaining crystallinity.

The main concerns and one of the most active areas of research at the moment are the utilization of visible light-sensitive photocatalysts for the degradation of organic contaminants like dyes, phenols, pharmaceuticals, brominated flame retardants, and other persistent organic pollutants (POPs). The application of SFNPs and their NCs can be easily recovered through an external magnetic field and repeatedly reused, making the process both cost-effective and environmentally sustainable, so the area requires proper attention. However, the majority of these studies focus less on the application to actual environmental samples and more on simulated experimental tests. It is necessary to conduct extensive research on the actual wastewater treatment in order for SFNCs to be used on a large scale in the future. Likewise, the motivation behind why the composite of at least two photocatalytic NPs manifest synergic impact on poison corruption isn't simply because of the lessening in energy band hole yet additionally because of the accessibility of various debasement courses and distortion of the SFNPs, the region actually expects top to bottom examination.

Photocatalytic activity

Absorption spectra were used to investigate the effect of nanoferrites on Rhodamine (RhB) photo-catalytic dye degradation. However, the photocatalyst's Eg determines the wavelength at which it absorbs light and generates electron-hole pairs. The nanoferrite specimens with the lowest Eg value were chosen for this study because they represent pure ferrite. This decision was made because the relationship between Eg and photodegradation behavior is opposite. In addition, the fact that ferrite replaces rare earth cations with good optical absorption in the visible range suggests improved photodegradation efficiency. For improving photocatalytic properties, the size of NPs, crystallinity, pollutant accessibility to the active surface, and organic pollutant diffusion resistance are all very important characteristics. In this regard, small particle sizes with high crystallinity are important because they have more active sites and a larger specific surface area, both of which favor increased photocatalytic activity. Particles with a high crystallinity can only be synthesized at high temperatures, which also increase the particle size. As a result, optimizing crystallinity without sacrificing particle size must be considered.

There is no standard reference photocatalytic material that could be used for comparison purposes for the new SFNCs-based photocatalyst, despite numerous studies on the improvement of synthesis methods for visible light-based photocatalytic materials. Doping various types of SFNPs with trace rare earth metals boosts photocatalytic capacity, as previously mentioned. However, tedious experimental work is typically required to optimize the stoichiometric ratio of metal ions that will be incorporated into SFNPs. The optimal amount of dopant that needs to be incorporated ought to be theoretically predetermined in order to cut down on time, money, and chemical waste. As a result, powerful software that facilitates the same task is required.

Photocatalytic application of SFNPs and SFNCs for wastewaterremediation

Worldwide concern stems from the presence of various contaminants in industrial wastewater discharge. Treatment and removal of toxic organic contaminants like dyes, phenols, chlorophenols, and nitro-phenols have been challenging for a very long time, especially when exposed to visible light. In wastewater treatment technology, metal oxides and semiconductors have gained a significant amount of attention for their photocatalytic degradation capacity of pollutants. Several studies have demonstrated the possibility of removing these contaminants through a photocatalytic approach using SFNPs, and this is the primary focus area of recent research. These photocatalysts must be stable and enduring under photoirradiation, which is an essential requirement.

It has been reported that the aforementioned properties of SFNPs and their NCs make them suitable for use as photocatalysts in wastewater treatment. One of the most cost-effective methods for wastewater treatment is the use of SFNCs as either an adsorbent or a photocatalyst. This is one of the most active areas of research right now. SFNPs easily convert visible light energy into chemical energy to support oxidation and reduction due to their low energy band gaps. Photocatalytic materials should be used to treat organic pollutants in wastewater so that they can be converted into other gaseous chemicals without causing waste, depending on the organic pollutants' elemental composition. As a result, the pho-tocatalytic degradation and removal of organic contaminants are regarded as eco-friendly, straightforward, and effective methods. The fact that SFNPs can be utilized as photocatalysts, in composites, and in the presence of oxidants like In fact, when combined with other light-sensitive strong oxidants and semiconductors, their high photodegradation capacity for pollutants is significantly enhanced. In this section, the mechanism of contaminant degradation caused by photocatalyst effects of SFNPs or their corresponding composites, as well as the advantages of SFNPs incorporation into semiconductors, particularly the reduction of corrosion, band gap, and electron-hole recombination, are briefly discussed.

CONCLUSIONS

Construction, morphology, and molecule size decide the synergist properties of spinel ferrites, and the manufactured strategies for the molecule manage these. Several well-known approaches to the synthesis of spinel ferrites have been discussed in this overview; The effect that various parameters have on particle size is also shown. The catalytic properties of spinel ferrites are outstanding. They have opened up a new avenue for researchers and have been confirmed as heterogeneous catalysts in organic synthesis. The photo-irradiated oxidation process's catalytic properties resulted in the successful degradation of various organic dyes. However, the catalytic properties of ferrites rise significantly when they are combined with other particles, such as those with a core@shell structure.

In general, the attractive physical and chemical properties of SFNPs, such as their stability and ease of surface modification with suitable semiconductors and organic moieties, make them a promising nanomaterial for addressing numerous generational challenges. In addition, despite numerous studies on SFNPs, the effects of incorporating various types of dopants are still poorly understood, necessitating the development of robust software that could assist in the theoretical prediction of possible combinations and their effects. In recent years, the incorporation of SFNPs attracted the attention of a number of researchers and was found to be a promising strategy for increasing their photocatalytic activities and magnetic separation. However, the commercialization of SFNPs-based photocatalysts appears to be hindered by resistance to departing from a well-established field.

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