

Photocatalytic Performance Enhancement Using External Magnetic Fields - A Review

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The coupling of external magnetic fields and photocatalysis has gained attention. However, the research in this field remains in nascent stages with unclear basic theory, mechanism and experimental method. The review aims to elucidate related basic theories, including the Lorentz force, spin polarization and radical pairs mechanism along with practical applications. One important factor restricting the application of external magnetic field in photocatalysis is the lack of robust characterization methods for spin detection, photo-generated electrons and holes detection and free radicals characterization. The challenges and prospects associated with the external magnetic field effect on photocatalysis are also discussed. This comprehensive review on the external magnetic field effect on photocatalysis, offering a detailed reference for understanding the coupling of external magnetic fields and photocatalysis and providing insight for the in-depth study.

1. Introduction

In the past decades, photocatalysis as a relatively mature advanced oxidation technology has been studied in various fields, such as photoelectrochemistry,^[1] semiconductor science,^[2,3] material science,^[4–6] and environment science,^[7] but also studied in pollutant degradation,^[8] water splitting,^[9] CO₂ reduction^[10] and organic compound synthesis.^[11] However, the relatively low efficiency of photocatalysis has limited the photocatalytic application in practical industrial production. This the primary research focus and the key issue that demands resolution. A classical photocatalytic reaction typically involves several crucial steps: (1) The catalyst is excited by incident light to generate electrons and holes; (2) separation of electrons and holes; (3) the reaction between carries and substance and (4) charge carriers react with dissolved oxygen, H₂O and O₂ to generate free radicals.^[12] Within

these steps, the intrinsic properties of conventional photocatalysts and charge carriers result in a low quantum efficiency of catalysts toward light and a high recombination rate of electrons and holes.^[13] Consequently, an increasing number of researchers are focusing on the development of new strategies to improve photocatalytic efficiency, for instance, developing novel catalysts or modifying catalysts make the catalysts can be excited by visible light or improve the quantum yield,^[14,15] applying an external electric field can reduce the recombination rate of electrons and holes.^[16] With the development of the preparation and modification of catalysts, researchers are increasingly turning their attention to external physical fields. The mainly studied fields

include electric field, thermal field, magnetic field, microwave field, ultrasound field and multiple fields combined. Each physical field's mechanism, application, and research progress are quite different. However, in general, photocatalytic reactions will be influenced when applying an external physical field by either injecting the energy of the field into reaction systems or altering the migration of electrons by external forces from the physical field.^[17] Therefore, research on the coupling of external fields and photocatalysis differs from traditional photocatalytic research, which focuses on the influence of the external field on the electrons, ions and free radicals rather than on the original redox reactions.

As more researches focus on the effect of external fields on photocatalytic reaction, a growing number of physical fields are being applied to enhance photocatalytic reactions. Common research fields include the thermal field, microwave field, electric field, magnetic field and ultrasound field. The principle of each field-enhanced photocatalytic reaction is different. The electric field enhances reactions through the electric polarization effect, wherein an external voltage drives particles with positive and negative charges to move directionally so that the electrons and holes recombination can be inhibited effectively. Alulema–Pullupaxi^[18] provided a detailed summary of the various factors influencing photoelectrocatalysis, including aspects such as reaction rig, catalyst types, contaminant types, and parameters (e.g., pH, voltage, electrolyte etc.) during the reaction. Liu et al.^[19] used TiO₂-CdS as a catalyst for the degradation of aqueous methyl orange via photoelectrocatalytic reaction. The results demonstrated that the degradation rate with an external electric field was 2.16 times

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higher than the degradation rate without an external electric field. Research on the effect of external fields on photocatalytic reactions has been in-depth and has even given rise to a new discipline, known as photoelectrocatalysis.^[18] The ultrasonic field assists photocatalytic technology and has attracted increasing attention. It is widely accepted that there are two primary mechanisms of photocatalysis enhanced by ultrasound: the cavitation effect^[20] and the piezoelectric effect.^[21] Sahand Jorfi et al.^[22] conducted a study that combined ultrasound and photocatalysis for the degradation of real sewage, utilize zeolite-loaded MgO NPs as a catalyst. The research proposed that the cavitation effect as the main principle has a significant contribution to the removal rate of chemical oxygen demand (COD) in real sewage. Additionally, the external physical process induces certain materials to generate a piezoelectric effect, which can be used to separate electrons and holes effectively to promote photocatalytic reaction rate. Wang^[23] et al. systematically reviewed the research progress of zinc stannate in the fields piezo-photocatalysis. They elaborated on the fundamental principles of zinc stannate-based piezo-photocatalysis and summarized various performance enhancement strategies addressing the challenges of rapid photo-generated charge carrier recombination and suboptimal piezo-photocatalytic activity. As for the coupling of microwave field with photocatalysis, there are other mechanisms to consider. The widely accepted theory is related to a unique thermal effect, where the microwave field can heat substances through the hot spot effect so that the microwave reduces the activation energy and change the reaction kinetics. Pang^[24] degraded the tetracycline hydrochloride (TCH) using ZnFe_2O_4 as the catalyst under the coupling of microwave and UV light. The degradation rate reached 91.6% in just 4 min which was far exceeding the degradation rate without the microwave. On the other hand, non-thermal effects are controversial, primarily due to technical limitations that hinder comprehensive testing. However, there are still some experimental results suggesting the non-thermal effect probably exists. Zhou et al.^[25] reported an experiment, which they irradiated semiconductor materials with microwave alone and on the semiconductor electric current and electron-hole pairs were generated. Despite this, there is still no clear theoretical explanation for this phenomenon, but the results seem to suggest the presences of some unknown non-thermal effects. Compared to magnetic fields, research on the other aforementioned external physical fields is relatively more mature, with numerous studies reported. Although these physical fields have been shown to enhance photocatalytic efficiency in various ways, each still has certain disadvantages that need to be addressed. For example, photoelectrocatalysis requires electrode fabrication and may produce photochemical side products during the catalytic process. Ultrasonic fields consume high energy and rely on the cavitation effect, which is difficult to control precisely. Furthermore, microwave fields tend to cause non-uniform effects. The effect of magnetic fields is also a subject of controversy. Mechanisms behind the synergistic effect of the magnetic field on the photocatalytic reaction mainly include the spin polarization effect,^[17] the free radical theory,^[26] and the Lorentz force effect.^[17] The specific theories will be introduced in the subsequent sections.

Several recent reviews have been published to provide meaningful guidance for the development of synergies between external physical fields and photocatalysis. For instance, Hu et al.^[16]

and Li et al.^[17] reviewed the principles of the external field and photocatalysis coupling, along with providing some general examples. However, these reports lack detailed discussion of each field. This review aims to give a detailed introduction to the synergy of magnetic field and photocatalysis, mainly including several mainstream theories, practical examples analysis, experimental rigs and relevant techniques. Our goal is that this review will provide a foundational reference for researchers in this field.

2. Theoretical and Experimental Studies of Magnetic Field Effect on Photocatalysis

In the introduction section, an overview of the basic photocatalytic reaction limitation and reaction mechanism, and the current research status on the effect of physical fields on photocatalysis were provided. We also discussed the current research status regarding the effect of physical fields on photocatalysis, with particular attention given to the magnetic field. Although some progress has been achieved, the mechanism of the coupling of an external magnetic field and photocatalysis has been studied and understood, and how magnetic field affects photocatalytic reaction is still controversial. Many researchers have proposed different theories and designed corresponding experimental equipment or modified the catalysts to elucidate the role of magnetic fields in photocatalytic reactions. In this section, we will summarize the existing theories and their associated experimental methods to create a comprehensive framework that combines theory and experimentation.

2.1. Lorentz Force

Reports pointed to that the Lorentz force induced by the external magnetic field can drive force to facilitate the separation of photogenerated electrons and holes by deviating the electrons' movement. In order to achieve this purpose, various strategies have been reported, for instance, synthesizing magnetic catalysts and building an experimental device that can drive the reaction solution to move directionally to meet the basic requirements of Lorentz force, namely a particle with charge moving at a velocity in a magnetic field experiences a force of $\vec{F} = q\vec{v} \times \vec{B}$.

In the context of a magnetic catalyst, the presence of an external magnetic field offers the ability to finely adjust the transfer and absorption of photo-generated electrons. Additionally, this magnetic field can effectively enhance the repulsion between particles, thereby inhibiting their aggregation. Furthermore, it can facilitate the attraction between the catalyst and reactant molecules, promoting their interaction. Lu^[27] et al. prepared magnetic $\text{CoFe}_2\text{O}_4/\text{MoS}_2$ heterojunction catalyst to degrade Congo red in the presence of an external magnetic field. As the external magnetic field intensity increased to 1500 Oe, the degradation efficiency reached 96.6%, attributed to a lower electron-hole recombination rate. Zhao^[28] et al. synthesized novel 3D/2D $\text{Mn}_2\text{O}_3/\text{g-C}_3\text{N}_4$ catalysts to remove nitrate and ammonia from water thoroughly by photocatalysis with the assistance of an external magnetic field. The Lorentz force not only drove the separation of the photogenerated charge but also increased the probability of NO_3^- -N and NH_4^+ -N collision with

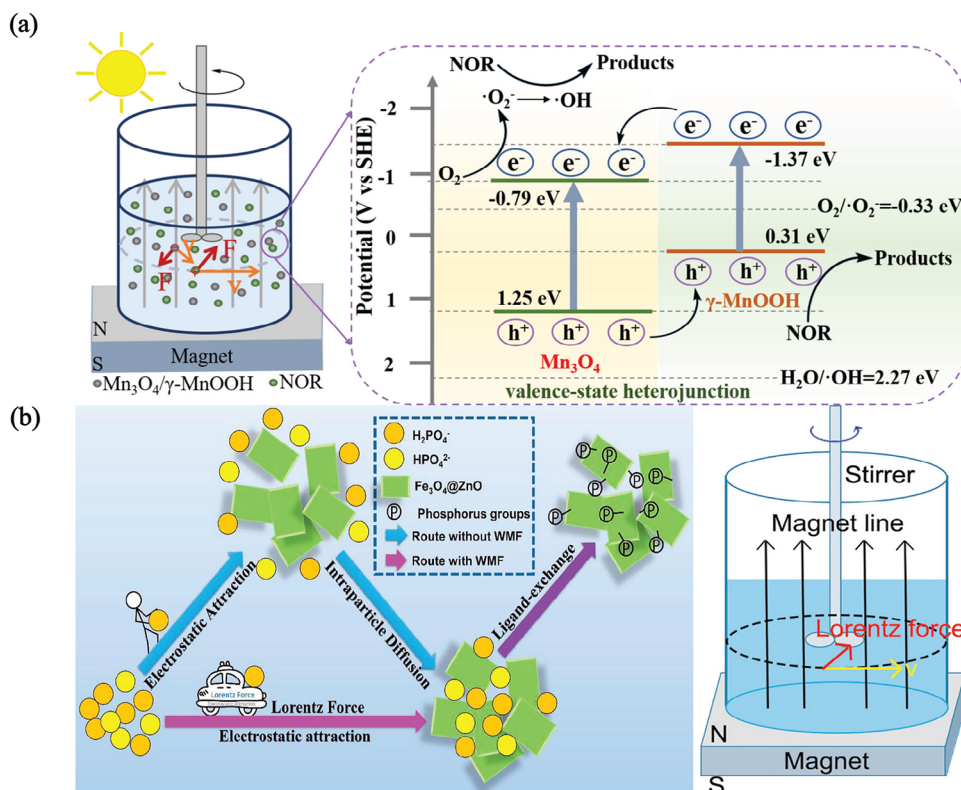


Figure 1. a) Schematic of weak magnetic field assisted photocatalytic degradation norfloxacin by using $\text{Mn}_3\text{O}_4/\gamma\text{-MnOOH}$ in a stirring setup. Reproduced with permission.^[30] Copyright 2025, Elsevier. b) mechanism and setup of 3D $\text{Fe}_3\text{O}_4@\text{ZnO}$ degrade phosphorus via weak magnetic field assisted. Reproduced with permission.^[29] Copyright 2025, Elsevier.

$\text{Mn}_2\text{O}_3/\text{g-C}_3\text{N}_4$. In addition to the direct utilization of magnetic catalysts, Li^[29,30] et al. have devised a method to facilitate the cutting of magnetic lines by the catalyst particles within an agitating system reactor. This approach effectively enhances the transfer of reactants. The reaction mechanism and schematic diagram of the equipment are shown in Figure 1. In all of these examples, the magnetic field was employed to enhance adsorption and improve the degradation rate by accelerating the movement of reactants toward the surface of the catalyst.

In addition to magnetic catalysts, some researchers have found that nonmagnetic catalysts can also be affected by external magnetic fields. Gao^[31] et al. designed a setup shown in Figure 2a, which applied permanent magnets beneath the photocatalytic reactor and used TiO_2 nanobelts as the catalyst to degrade methyl orange. Upon introducing the permanent magnets into the reaction system, the photocatalytic degradation of methyl orange increased by 26% in comparison to degradation in the absence of permanent magnets. Especially, as the agitation speed and magnetic field intensity increased the degradation kept on increasing. Based on the above experimental results, Gao et al. concluded that these results were due to the effect of Lorentz force on photo-generated electrons and holes. By observing the relationship between degradation, magnetic field intensity and agitation speed, they found that increasing the stirring speed and magnetic field intensity led to the accelerated movement of electrons and holes in the magnetic field, consequently increasing the Lorentz force and reducing the recombination rate of electrons and holes. Be-

cause of the opposite charge of electrons and holes, when electrons and holes move in a magnetic field, the electrons and holes will experience opposite orientation forces so that electrons and holes can be separated efficiently, shown in Figure 2b,c. Gao et al. believed that the catalysts particle were in the movement along with the suspension in the magnetic field aligning with the stirring orientation. Increasing the agitation speed and magnetic flux will lead to an increase of \vec{v} and \vec{B} so the Lorentz force on electrons increases which can inhibit the recombination of electrons and holes further effectively. Li^[29] et al. used Lorentz force drive to enhance the absorption of phosphorus on the 3D $\text{Fe}_3\text{O}_4@\text{ZnO}$ nanocubes in the presence of a weak magnetic field. Similarly, Huang^[32] et al also considered using Lorentz force to improve the photocatalytic performance. In this research, a micro optofluidic chip reactor was built as shown in Figure 2d,e. Weak external magnetic fields (100-1000Oe) were applied to enhance the photocatalytic degradation of methyl orange by using TiO_2 nanoparticles as a catalyst within the reactor. The rectangular channel and TiO_2 deposited on the glass substrate can control the reaction enhancement by magnetic field in a specific orientation. Additionally, the effects of dissolved oxygen and hydroxyl ions were studied in the presence of the magnetic field. The experimental results revealed that the 1000Oe normal magnetic field (Figure 2 left) increase the degradation of MO 1.78-fold, which is different from the above results, two pairs and four pairs of neodymium magnets were placed laterally respectively, and the degradation of MO increased compared to the normal placement. Therefore,

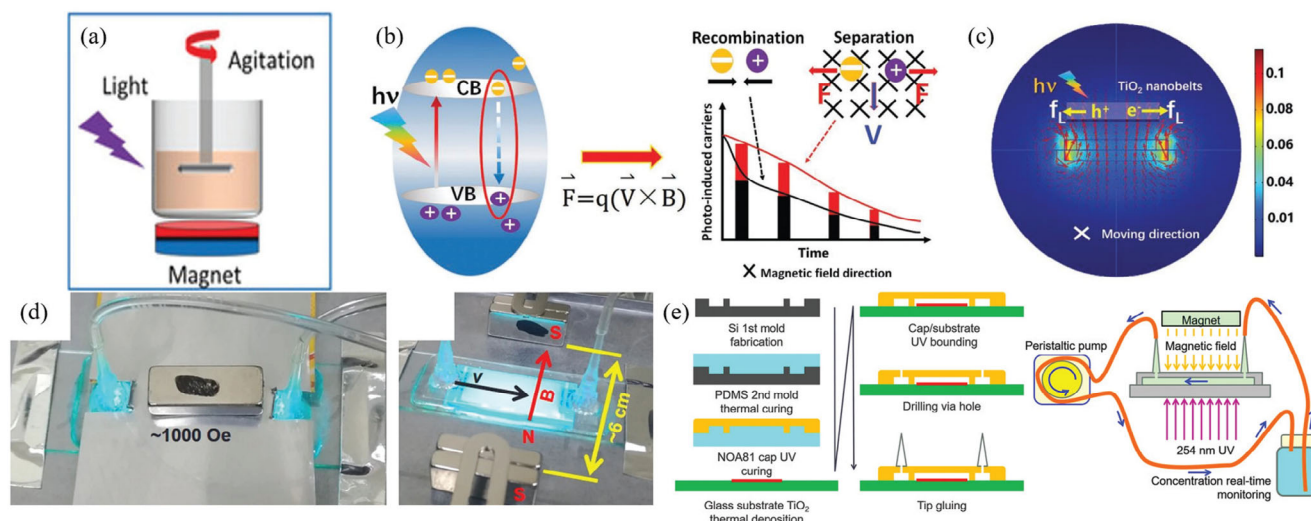


Figure 2. a) Schematic diagram of the magnetic field photocatalytic setup.^[31] b) Schematic illustration of the proposed influence of the magnetic field on photoinduced charge carrier separation in the TiO₂ nanobelts.^[31] c) Schematic diagram of the interaction between the magnetic field and the moving photocatalyst under illumination.^[31] Copyright 2025, John Wiley & Sons. d) Experimental setup under a normal magnetic and lateral magnetic field.^[32] e) Schematics of the chip fabrication process and the experimental setup. Copyright 2025, Springer Nature.^[32]

the author suggested that the lateral placement was better than the normal placement. These results also provide a novel perspective on how the location of the magnetic field may affect the photocatalytic performance. Furthermore, the concentration of dissolved oxygen also strongly affected the degradation efficiency in the presence of the magnetic field. The author noted that the generation and mass transfer rate of OH⁻ increased significantly when the magnetic field was introduced.

The above paper reported the practical applications and experimental designs aimed at improving photocatalytic performance by Lorentz force. By driving the movement of photogenerated electrons in the magnetic field to prevent electrons and holes recombination. A common feature of these reactors is to make the reaction suspension move along the vertical direction of the magnetic field to cut the magnetic inductance line. The strength and direction of the magnetic field also affect the photocatalytic efficiency. In addition to the above mechanisms, Lorentz force also can improve the absorption of target objects and catalysts.

2.2. Spin Polarization

Spin is the intrinsic angular momentum of electrons, and spin polarization refers to the degree to which spin orientations are aligned with a given direction.^[33] Electrons have two spin states, spin-up and spin-down. When slight energy is introduced into the reaction, the electron's spin orientation will flip, and this transition in the spin state will have an effect on catalytic performance.^[34] Numerous spintronics devices have been developed to facilitate spin transport in solid materials. This is achieved by generating and injecting spin flow or by manipulating the spin-polarized population of electrons within the material.^[35] If the spin-up and spin-down states of electrons are present in equal measure, spin transport cannot occur. So it is necessary to generate net spin in solid catalysts. Zhang^[36,37]

et al. proposed the spin polarization phenomenon to explain the enhancement of magnetic field effects on photocatalysis. They suggested that the spin polarization caused by an external magnetic field can effectively inhibit electron and hole recombination. However, due to the research limitation, the authors did not give a detailed explanation. With further research, it has been demonstrated that spin polarization can indeed enhance photocatalytic performance. When an excited electron is in the conduction band, it can only be captured by holes if the holes have opposite spin orientations to the excited electrons, as dictated by the Pauli exclusion principle.^[38] The schematic illustration is shown in Figure 3.

Currently, some scholars have improved the photocatalytic performance of catalysts by manipulating the spin polarization of the catalysts. Various strategies are used to induce spin polarization and transportation, including: (1) heavy atom induced charge intersystem crossing relaxation.^[39–41] This mechanism is based on the idea that heavy atoms, such as graphene, can break spin-forbidden rules. (2) Heavy atoms can induce electron spin-flip and tunneling. When the p or f orbitals of a heavy atom are fulfilled, they can form hybrid orbitals with the two-dimensional transfer medium. The transferred electrons can then tunnel through the 2D transfer medium by jumping over these hybrid

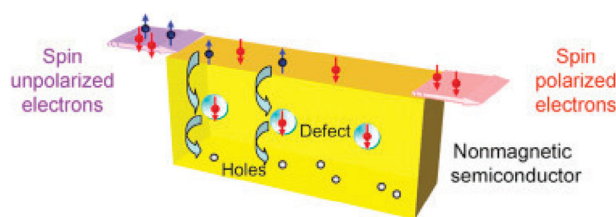


Figure 3. Schematic of electrons capture and recombination in the condition of spin polarization. Copyright 2025, Elsevier.^[38]

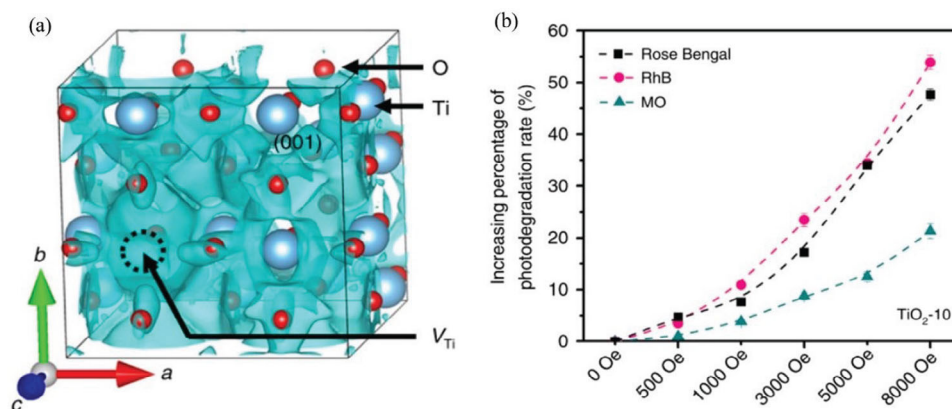


Figure 4. a) the model of $\text{Ti}_{15}\text{O}_{32}$ cell. b) the degradation rate of $\text{TiO}_2\text{-10}$ under different magnetic field intensities from 0 to 8000 Oe. Copyright 2025, Springer Nature.^[50]

orbitals. (3) Magnetic field induction, the magnetic field can enhance the electron transport by inducing spin polarization^[42] and align the spin orientation and hybridize orbits.^[43,44] And some other methods, such as, utilizing the ability of chiral molecules to filter the spin states of electrons in order to achieve spin polarization,^[45–47] utilizing the special surface conducting of topological insulators to induce spin transfer.^[48,49]

In the following section, we will introduce several studies focused on improving photocatalytic efficiency by manipulating the spin polarization of catalysts. Li^[50] et al. conducted a study in which they modified TiO_2 and introduced a magnetic field to the photocatalytic reaction. They demonstrated a controllable method to manipulate the spin polarization of TiO_2 by altering the concentration of Ti vacancies and measured the photocatalytic performance of the resulting material under a magnetic field. Characterization results indicated that changing the concentration of Ti vacancies led to spatial spin polarization, as illustrated in **Figure 4a**. The use of this type of material as a catalyst showed that the magnetic field had a significant influence on the

photocatalytic reaction, **Figure 4b**. Li explained that a magnetic field can enhance polarization, thereby preventing the active substance from recombining. This study offers new insights into the design of magnetic field-responsive photocatalytic materials with enhanced performance. Through simulations and density functional theory (DFT) calculations, it demonstrates that an external magnetic field can enhance spin polarization, thereby effectively suppressing the recombination of photogenerated electron–hole pairs. However, the analysis of spin polarization in this work relies primarily on theoretical simulations, with a lack of evidence through experimental characterization techniques. As a result, the conclusions drawn remain insufficiently supported by experimental evidence.

Gong^[51] et al. synthesized the COF-367-Co, in which the spin state of cobalt can be manipulated by controlling the oxidation state of Co. As shown in **Figure 5a**, COF-367- Co^{III} exhibited higher activity and selectivity to HCOOH than COF-367- Co^{II} , accordingly reduced activity and selectively to CO and CH_4 . In **Figure 5b**, by changing the chemical state of Co from +2 to

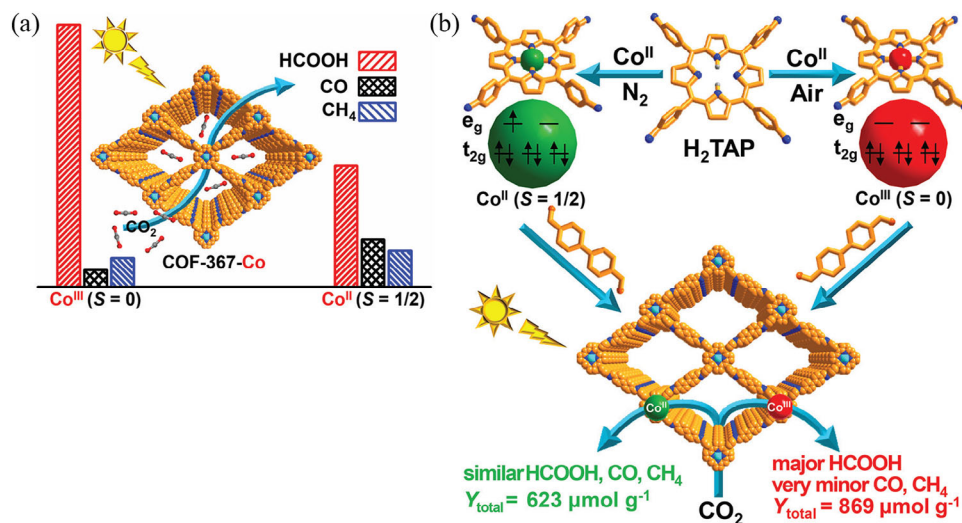


Figure 5. a) Schematic illustration of COF-367- Co^{III} and COF-367- Co^{II} degrade CO_2 process. b) COF-367-Co featuring different spin stats of Co toward CO_2 reduction. Copyright 2025, American Chemical Society.^[51]

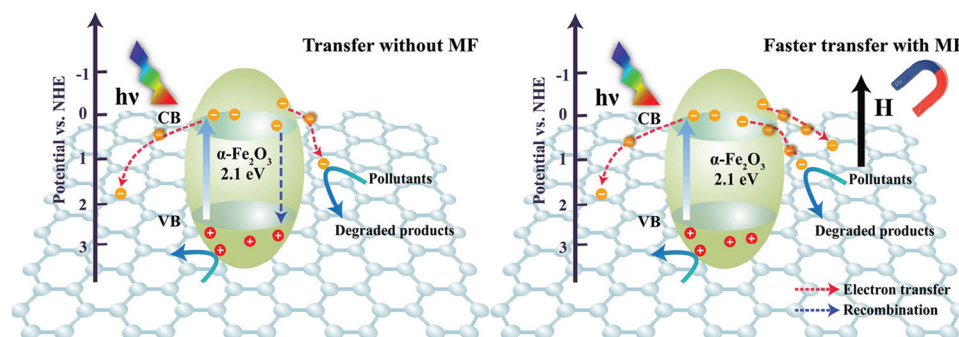


Figure 6. Schematic illustration of the mechanism of the $\alpha\text{-Fe}_2\text{O}_3/\text{rGO}$. Copyright 2025, American Chemical Society.^[56]

+3, the spin state changed from $S = 0$ to $S = 1/2$. Therefore, this demonstrated that changes in spin states can lead to variations in the performance of catalysts. Tong^[52] et al. manipulated spin state transition by controlling the lattice orientation of LaCoO_3 films, which change the electrons' occupancy. In this case, LaCoO_3 (100) film shows optimal e_g electron filling and better oxygen evolution reaction performance than LaCoO_3 (110) and LaCoO_3 (111). Maher^[53] et al. reported that bilayer graphene exhibited antiferromagnetic behavior, but transitioned to a ferromagnetic phase when exposed to a magnetic field of 27.5 T. This report highlights the potential of magnetic field-induced electron polarization to enhance photocatalytic performance. Gao^[43] et al. investigated the effects of an external magnetic field on the Suzuki cross-coupling reaction using a $\text{Pd}@\text{Co}_3[\text{Co}(\text{CN})_6]_2$ catalyst. They discovered that the 2p orbital of carbon on the bromobenzene and the 4d orbital of palladium overlapped more closely and that the hybridization between the Pd d-orbital and C p-orbital was enhanced under the magnetic field. This improved hybridization is beneficial for facilitating electron transfer from Pd to bromobenzene.

The examples above demonstrate various approaches to manipulate the spin state of catalysts through catalyst modification. Although there have been some reports supporting spin polarization theory within the field of photocatalysis, such as Li's study attempting to manipulate the spin state of photocatalysts, research in this area remains relatively limited. Therefore, to broaden the range of methods for spin state modulation, drawing on approaches from other related fields may prove valuable. Further investigation is required to develop more efficient strategies for controlling the spin states of photocatalysts in the future.

In addition, there is a type of magnetoresistance (MR) known as magnetically induced spin polarization resistance. This phenomenon is observed in certain ferromagnetic metals that can be used in magnetic nanostructures. When an external magnetic field is applied to such a material, it induces a spin polarization effect, which leads to a change in the carrier migration properties and the resistance of the catalysts.^[54,55] The negative MR effect is a phenomenon in which the electrical resistance of a material decreases when an external magnetic field is applied. In the context of a photocatalytic reaction, this effect implies that the photo-generated charge carriers will migrate faster, which helps to separate the electrons and holes, and more carriers will take part in surface reactions. Li^[56] et al. synthesis $\alpha\text{-Fe}_2\text{O}_3$ reduced graphene oxide ($\alpha\text{-Fe}_2\text{O}_3/\text{rGO}$) to improve the photocatalytic re-

action in the presence of a magnetic field by using the property of negative MR effect. The degradation of RhB in the presence of a magnetic field was 1.75 times higher than that in the absence of a 6 kOe magnetic field. In the presence of an external magnetic field, the magnetic moments of $\alpha\text{-Fe}_2\text{O}_3$ and rGo were parallel alignment which resulted in a negative MR effect. The application of an external magnetic field resulted in an increase injection rate of carriers from $\alpha\text{-Fe}_2\text{O}_3$ to rGo, ultimately leading to an increase in RhB degradation. The schematic diagram of the reaction mechanism is shown in Figure 6.

This section introduces the application of spin polarization in photocatalysis, as well as the phenomenon of spin polarization enhanced by external magnetic fields. It also presents various methods and studies for achieving spin polarization and spin migration. Magnetic fields play a crucial role in the spin polarization phenomenon and can effectively promote it. They not only align the spin orientation of electrons to enhance spin polarization but can also induce materials to become ferromagnetic. However, it is important to note that the spin polarization theory remains in its infancy within the field of magnetic field–photocatalysis coupling. While some researchers have employed spin polarization theory to explain the enhancement of photocatalysis by magnetic fields, there is a lack of direct experimental evidence supported by characterization methods. Furthermore, research on how to modify catalysts to manipulate spin states in this field is still limited. Therefore, future studies should focus on these two key aspects.

2.3. Radical Pairs Mechanism

Moreover, apart from the properties of the catalysts, free radicals play a significant role in determining the efficacy of a photocatalytic reaction. These free radicals could be photo-generated electrons, hydroxyl radicals, super-oxide radicals, and various other types of free radical particles. Thus, investigating the migration and transformation of these free radicals during the reaction is crucial. When photons strike precursors, electrons get excited and transition from the valence band to the conduction band, generating free radicals. Typically, the free radicals produced are singlet RPs (S_1) due to the forbidden transition between the ground singlet state electrons (S_0) and the excited triplet state electrons (T_1). The likelihood of generating triplet excited electrons in this process is merely 10^{-5} . The RPs produced in the

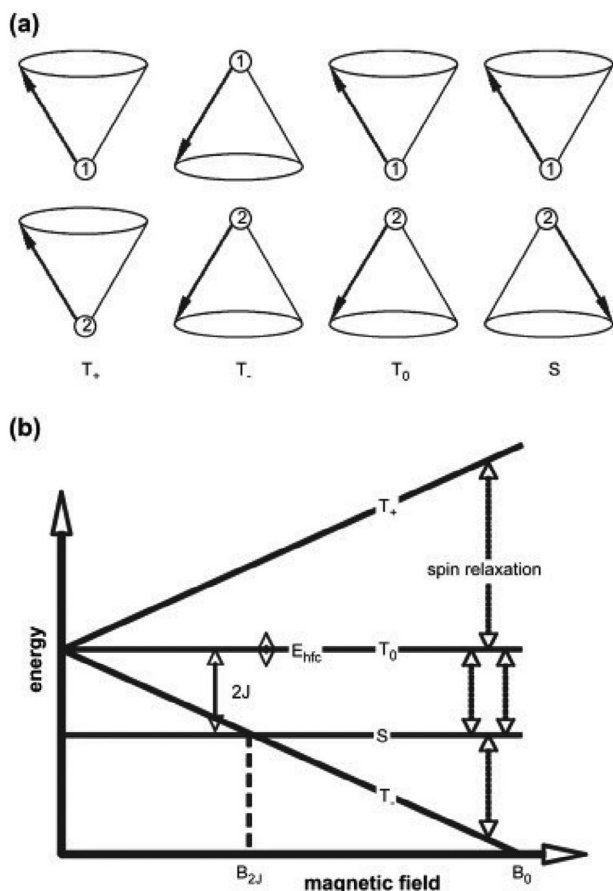


Figure 7. a) Vector of the singlet and triplet states. b) The function of Zeeman energy and magnetic field intensity. E_{hfc} is the hyperfine coupling energy and J is the singlet-triplet transition energy. Copyright 2025, American Chemical Society. Copyright 2025, Elsevier.^[58,59]

aforementioned process undergo inter-system crossing to produce triplet radicals or back reactions to regenerate precursors. The triplet radicals then undergo similar reactions with singlet radicals.^[57] The vector representation of singlet and triplet is shown in Figure 7a. As reactions typically occur in a solution environment, the cage effect is a factor that requires consideration. The cage effect also affects the lifetime of free radicals. During a reaction process, the generated free radicals form pairs that create an initial cage with solvent atoms. If radical transformation reactions take place inside the cage, it is known as a cage reaction, and the resulting product is called cage production. Conversely, if the reaction occurs outside the cage, the product is commonly referred to as escape production. A fundamental principle in magneto-chemistry is that the recombination of free radicals can only occur between singlet radicals. Thus, it is generally believed that the magnetic field can alter the spin state of free radicals, inhibiting the recombination of electrons and holes and prolonging the lifetime of free radicals.

When the electrons are exposed to a magnetic field B_0 , the energy of electrons' states can be expressed as $E = g\beta B_0 \sum S_z$, where g is the dimensionless electron g factor, β is the Bohr magneton, $\sum S_z$ is the sum of spin contribution in the direction of the magnetic field. Figure 7b illustrates the energy of various spin

states. The Zeeman energy of each spin state can be represented as follows: E_S (singlet) = 0, $E_{T+} = g\beta B_0$, $E_{T-} = -g\beta B_0$ and $E_{T0} = 0$. The E_{T+} and E_{T-} are positively or negatively correlated with the intensity of the magnetic field. E_{T0} and E_S remain unaffected by external magnetic fields, while E_S is completely independent of the magnetic field and E_{T0} has a non-zero component in a direction perpendicular to B_0 . For these spin states, the singlet state is more likely to cause radicals combination, while triplet states are not. Through the above discussion, singlet and triplet states can interconvert during reactions. However, an external magnetic field can split the triplet states and reduce the probability of the triplet-to-singlet transition.^[60]

3. Characterization Method for the Magnetic Field Effect in Photocatalysis

Characterization methods play a vital role in elucidating the intrinsic mechanisms of magnetic field-enhanced photocatalytic reactions and assessing the performance of catalysts. The Table 1 shows the commonly used characterization methods in photocatalytic research. In addition to commonly used methods such as XRD and TEM, this section will review some specialized techniques related to free radicals, their lifetime, and spin.

3.1. Spin Detection

Since spin is a quantum property characterized by angular momentum, the flip of an electron's spin results in a slight change in angular momentum, which can be converted to a small change in mechanical torque. A spin detection method was developed based on this principle. Figure 8 illustrates a typical nano-scaled torque-shaped spin mechanical device used for spin detection.^[72] It is composed of nanoscale materials such as nanosheets and nanowires to form a torsion oscillator. Nanoscale torsional oscillators can sensitively respond to the flipping of spin electrons. Furthermore, by observing the direction of torsional oscillation, the direction of spin flipping (up or down) can be determined.

Utilizing tunneling barrier penetration, constructing tunneling contacts is considered a feasible and robust method for detecting spin polarization. Figure 9a–d depicts several tunnel contact devices consisting of a tunnel barrier, ferromagnetic material, and non-magnetic material.^[73–76] These tunnel contacts include two-terminal configurations (Figure 9a,c), nonlocal measurements (Figure 9d), and three-terminal (Figure 9b). These devices utilize the mechanisms of the local magneto-resistance effect, Hanle effect, and non-local spin transport, respectively, to detect the spin state. Tunnel contact devices are good tools to detect

Table 1. Characterization techniques for photocatalysis.

Purpose	Common Devices
Structure analysis	XRD, ^[61,62] X-ray absorption spectrum (XANES), ^[50] TEM and SEM ^[63,64]
Elements Composition	EDS, XPS, ^[65,66] ICP-MS and ICP-AES
Spin detection	ESR ^[15,67]
Optical property	UV-vis-NIR Spectrometer ^[68–70]
Intermediate products	GC/LC-MS ^[71]

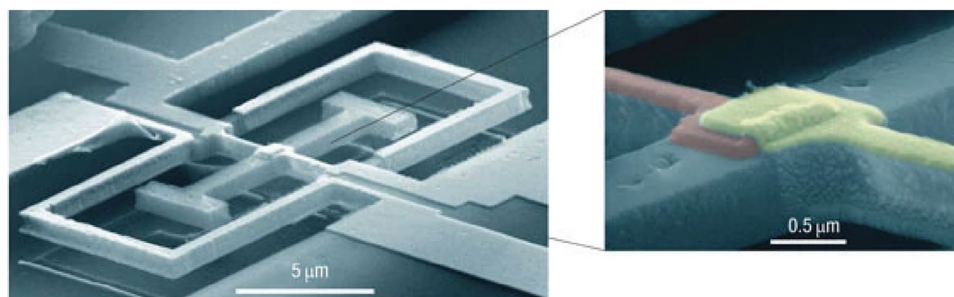


Figure 8. Scheme of a single-crystal silicon torsion oscillator. Copyright 2025, Springer Nature.^[72]

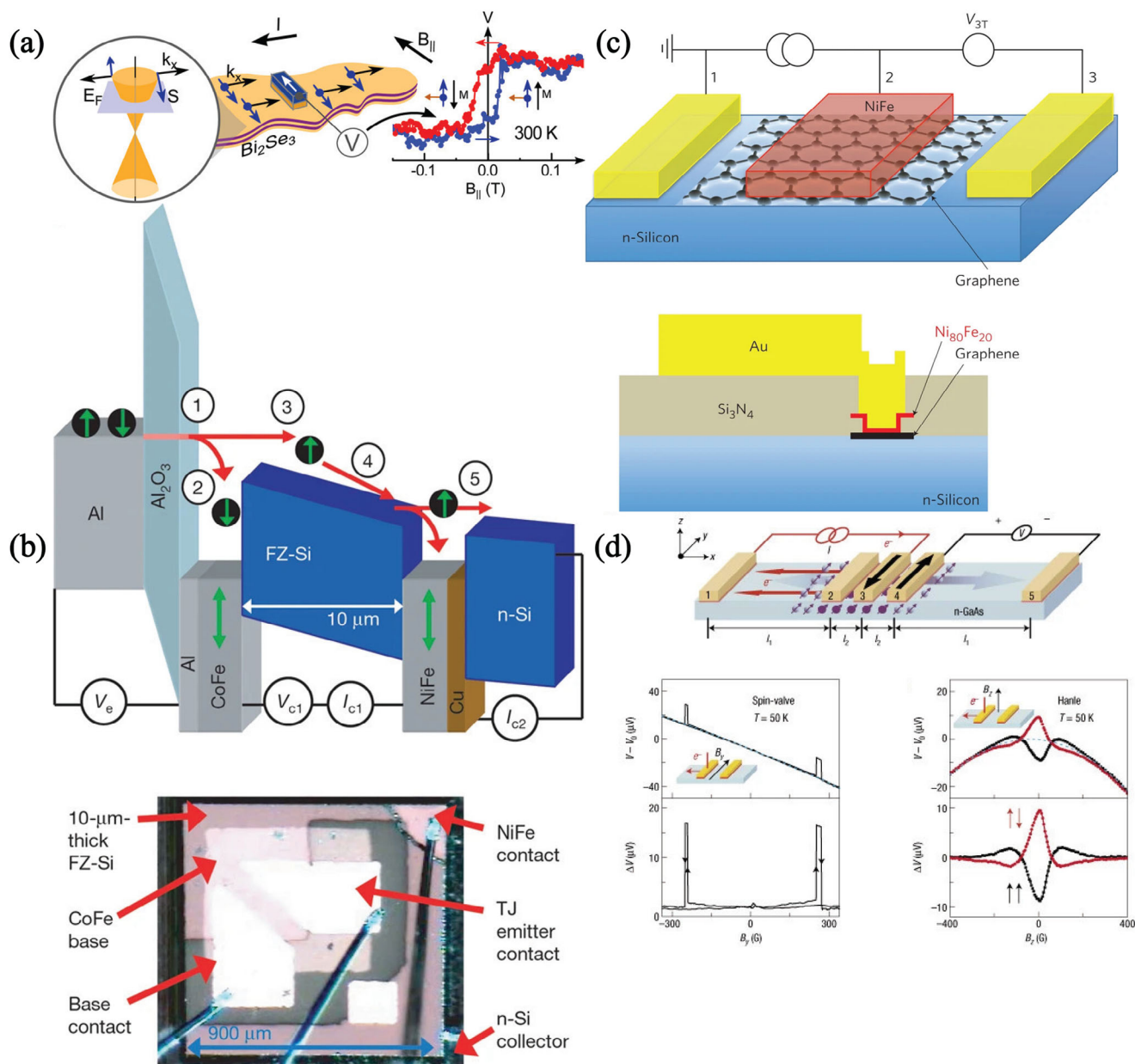


Figure 9. a) Schematic of spin valve device to probe the spin helical topological surface states.^[73] Copyright 2025, American Chemical Society. b) Illustration of the Si spin transport device.^[74] Copyright 2025, Springer Nature. c) Monolayer graphene serves as a tunnelling barrier between ferromagnetic metal contacts and a silicon substrate.^[75] Copyright 2025, Springer Nature. d) Schematic of the non-local spin valve and Hanle effects. Copyright 2025, Springer Nature.^[76]

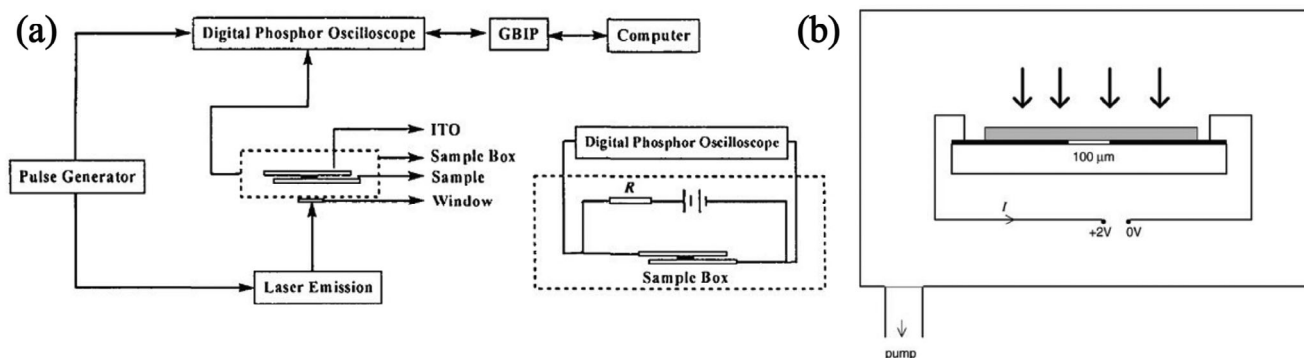


Figure 10. a) Schematic diagram of the setup for surface photoconductivity measures;^[36] Copyright 2025, Royal Society of Chemistry. b) Schematic of a device structure for photoconductivity measurements in air and vacuum. Copyright 2025, Elsevier.^[79]

the spin state, spin lifetime, transportation and diffusion length. Parkin^[77] et al. used MgO tunnel barriers and the 3-T Hanle technique to study the spin lifetime and spin transportation of lanthanum and niobium-doped SrTiO₃. The results show that the shorter spin lifetime observed in SrTiO₃ is attributed to the formation of Ti³⁺ defects within SrTiO₃.

These two methods are currently well-established and commonly used for detecting the spin state of catalysts. Based on the introduction in the Section 2, magnetic fields can influence the spin polarization, spin state, and spin transportation of catalysts. Therefore, the methods described in this chapter can be used to detect the impact of magnetic fields on catalyst spin properties, thereby analyzing the principles of magnetic field effects in photocatalysis.

3.2. Photogenerated Electrons and Holes Detection

Electrons and holes are the most important substance in the photocatalytic reaction and are the basis of all redox reactions.^[78] The magnetic field can affect the generation and migration of electrons and holes, so it is necessary to find suitable methods to verify the above hypothesis. Transient absorption spectroscopy is one of the commonly used methods to characterize the kinetics of electrons and holes. Transient Absorption (TA) spectroscopy is a pump-probe spectroscopic technique used to measure the energy and associated lifetimes of excited states in molecules, materials, and devices. The pump-probe technique can be described as the excitation of a sample by a light source (pump pulse) and the measurement of absorption changes of a second light source (probe pulse) as a function of wavelength and time. The focus of this technique is to measure excited singlet and triplet states, electron and energy transfer mechanisms, as well as photoproduct reactions. Transient absorption spectroscopy enables the characterization of the relationship between recombination and time at a specific wavelength, as well as the relationship between wavelength and recombination at a specific time. However, when investigating the coupling of magnetic field and photocatalysis, a limitation arises due to the inability to apply an external magnetic field.

To enable the detection of electron-hole recombination of the reaction under the application of an external magnetic field, we introduce a system designed by Nelson^[79] and Zhang^[36] et al., the

system is to study the photoconductivity to figure out the photo-generated electrons and holes recombination process, shown in **Figure 10**. The photocurrent can be attributed to the electron density in the conduction band and can be quantitatively described using rate equation models that trapping, recombination, and scavenging. **Figure 11** shows the photoconductivity spectrum of Pt/TiO₂ under different magnetic field intensities. It is found that as the magnetic field intensity increases, the recombination rate of electrons and holes decreases, resulting in an increase in the lifetime of charge carriers. Since this system was a custom-made device, it allowed for the flexible application of an external magnetic field. However, in practical applications, the use of self-made equipment may introduce complexity.

3.3. Free Radicals Characterization

In addition to studying photogenerated electrons and holes, an equally important substance in photocatalytic reactions is free radicals. Free radicals also exert a significant influence on photocatalysis. To investigate the impact of radicals on photocatalysis, numerous scholars employed various methods to explore the migration and transformation of free radicals during the

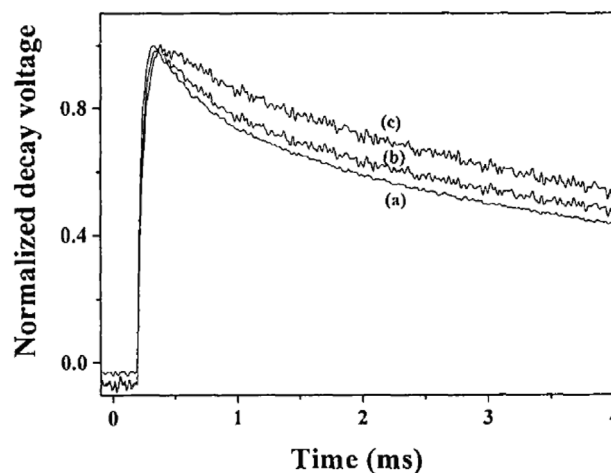


Figure 11. The influence of magnetic field on decay voltage under different magnetic field intensity, a) no magnetic field, b) 25.1 mT, and c) 85.7 mT.^[36]

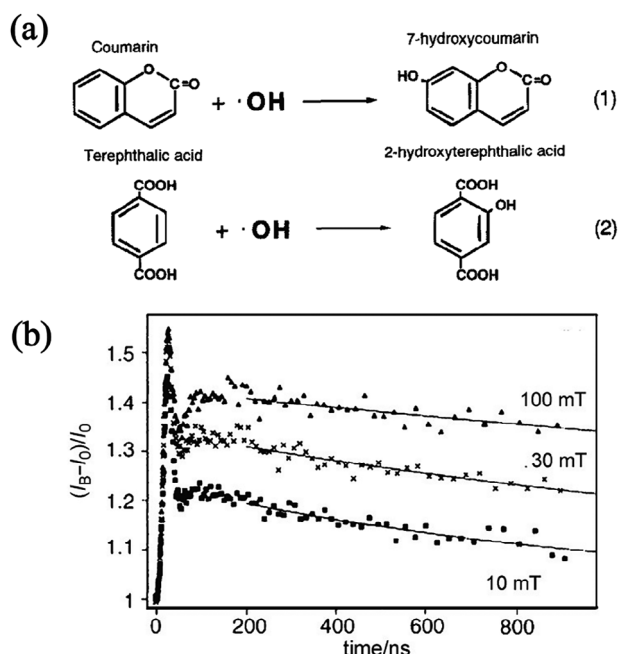


Figure 12. a) (1) reaction between hydroxyl oxide and coumarin, (2) reaction between hydroxyl oxide and terephthalic acid. b) Field effect on fluorescence decays of p-terphenyl in squalane excited by 90Sr b-particles. Copyright 2025, Elsevier. [80]

photocatalytic process. The two commonly used method is fluorescence. Fluorescence spectroscopy is a method for analyzing the concentration of a substance by detecting the fluorescence emitted by the substance. When detecting free radicals using fluorescence spectroscopy, it is generally necessary to select appropriate scavengers/capture agents. For example, one of the most important free radicals in photocatalysis, the hydroxyl radical, can be effectively captured by coumarin, the reaction is shown in **Figure 12a**. The concentration of hydroxyl radicals can be determined by detecting the fluorescence intensity emitted by 7-hydroxycoumarin. Kenichi^[80] et al. used coumarin and terephthalic acid as capture agents to test the hydroxyl radicals produced on TiO_2 photocatalyst in an aqueous solution. The related reactions are shown in **Figure 12**.

The fluorescence method not only enables the identification of the types of free radicals present in a solution but also allows for the characterization of their decay. In a review by Brocklehurst,^[81] the fluorescence method was employed to measure the decay of free radicals in the presence of a magnetic field, along with corresponding theoretical explanations. As illustrated in **Figure 12(b)**, there is a noticeable decrease in the decay of fluorescence intensity with increasing magnetic field intensity, indicating that the magnetic field potentially prolongs the lifetime of free radicals.

The above content primarily reviews various detection methods for the spin state, electron-hole recombination process, and free radicals' lifetime and migration. Due to the nano-scale property of these parameters or their extremely rapid recombination rates, the detection of these characteristics poses significant challenges. Additionally, when an external magnetic field is applied, some commonly used devices may not be able to detect the effect of the magnetic field on the photocatalytic reac-

tion, such as the transition absorption spectroscopy. Therefore, homemade devices are detailed introduced in this section. The detection techniques for the above target are still under extensive research. Consequently, the precise detection of spin states, electron-hole recombination, and free radical lifetimes remains an important topic in the study of the coupling between magnetic fields and photocatalysis.

4. Challenges and Perspective in Magnetic Field Enhanced Photocatalytic Reaction

In this review, the mechanism of the magnetic field effect, the latest research and related applications have been summarized. As an integrated system, the magnetic field induces more energy into a photocatalytic reaction, acting as a driving force to efficiently inhibit the electrons and holes recombination. First, some related mechanisms are reviewed in this paper, including free radical pairs theory, hyperfine theory, δg mechanism, Lorentz force, etc. Then the setup and system of magnetic field-assisted photocatalysis and some latest research and practical application are also introduced. Even though the magnetic field increases the complexity of the setup, characterization and analytics, the combination of magnetic field and photocatalysis forms a new interdisciplinary discipline that can expand the boundary of photocatalysis, develop new theories and promote the application of photocatalysis in practical industry. However, there are still some problems that need to be solved and theoretical gaps to supplement. How to quantitatively analyze the relationship between the magnetic field and photocatalysis even chemical reactions so that can maximize the use of magnetic field are still barriers. In conclusion, the magnetic field-assisted photocatalysis system has been well demonstrated in this review. Till now, some progress has been got and some problems need to be solved. For future work, the research on the link of magnetic field and microscopic mechanism of electron and hole recombination and transfer process should be a key point.

In terms of the mechanism, several theories have been proposed to explain the magnetic field effect on photocatalysis, like Lorentz force, Zeeman effect, radicals pair theory, etc. However, there is still controversy surrounding these theories. The reason for these controversies is also attributed to the immaturity of characterization methods. For example, in the above section, the characterization of the catalyst spin state has been explored by some researchers. However, due to the complexity of characterization methods, achieving efficient and accurate characterization remains challenging. This also implies that theories related to spin theory lack corresponding characterization data for support. Doping with paramagnetic elements or introducing magnetic metals/oxides to construct heterojunctions has been studied, with the aim of inducing or enhancing electron spin polarization on the material surface, thereby improving the photocatalyst responsiveness to magnetic fields. However, as discussed in this paper, even non-magnetic or unmodified catalysts can be influenced by magnetic fields, and the underlying mechanism has also been attributed to spin polarization. The explanation that magnetic fields enhance photocatalytic efficiency by increasing the spin polarization of photogenerated charge carriers remains to be thoroughly investigated. This issue involves complex quantum mechanical

theories and requires validation through advanced characterization techniques. The precise relationship between the degree of spin polarization and magnetic field strength also warrants further study. Another issue concerns the active species involved in the process, such as the photogenerated electron-hole pairs and free radicals like hydroxyl radicals. Due to their low concentrations and short lifetimes, it becomes challenging to observe and characterize them accurately.

Although the application of external magnetic fields has shown potential in enhancing photocatalytic efficiency, the extent of this enhancement remains limited, and the utilization efficiency of the additional energy input in photocatalytic reactions has not reach an ideal level. As discussed earlier, some studies incorporated small permanent magnets into the reaction setup or synthesized magnetic materials to enable photocatalysts to respond to magnetic field and thereby improve their photocatalytic performance. However, comparable enhancements can also be achieved through alternative approaches that require fewer resources. Therefore, integrating multiple reaction mechanisms to simplify the system and minimize external energy input while effectively harnessing magnetic energy may represent a promising future direction. Realizing this goal requires elucidating the underlying “black box” mechanism and establishing a clear quantitative relationship between the magnetic field dynamics and the microscopic mechanisms of charge transport. Achieving this will rely on advanced in situ and time-resolved characterization techniques, along with systematic theoretical analysis, to gain a deeper understanding of how magnetic fields influence the photocatalysis. Consequently, further research is needed to demonstrate how magnetic fields affect the generation, migration, transformation, recombination, and lifetime of these free radicals.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

P.L. contributed to the conceptualization, formal analysis, and investigation of the study, and was responsible for writing the original draft as well as reviewing and editing the manuscript. X.M. contributed to the conceptualization and participated in the review and editing of the manuscript, while also providing supervision. J.G. also contributed to the conceptualization, manuscript review and editing, and provided supervision throughout the project.

Keywords

External magnetic field, Lorentz force, Photocatalysis, radical pairs mechanism, spin polarization

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