Chapter

Tuning the Magnetic and Photocatalytic Properties of Wide Bandgap Metal Oxide Semiconductors for Environmental Remediation

Ganeshraja Ayyakannu Sundaram, Rajkumar Kanniah and Vaithinathan Karthikeyan

Abstract

The review focuses on recent developments towards preparing room temperature ferromagnetic metal oxide semiconductors for better photocatalytic performance. Here we reported the combined study of photocatalytic and ferromagnetic properties at room temperature on metal oxides, particularly TiO_2, which is rapidly an emerging field in the development of magnetism and environmental remediation. Even after decades of research in this area, the exact mechanism of the combination of ferromagnetism and photocatalysis in these materials has been not understood completely. However, some of the critical factors were hinted about the contribution to magnetism. Many reports demonstrated that oxygen vacancy and various metal doping plays a primary role in the room temperature ferromagnetism and photocatalysis in wide-band-gap metal oxides. However, it is not easy to understand the direct correlation between magnetism, oxygen vacancies, dopant concentration, and photocatalysis. This review primarily aims to encompass the recent progress of metal oxide for understanding magnetism and photocatalyst under visible light.

Keywords: metal oxide, titania, ferromagnetism, photocatalysts, semiconductors

1. Introduction

The optical, magnetic, and photocatalytic properties of wide bandgap metal oxide semiconductors (MOS) are easily tunable by adjusting the defect concentration, attaining great attention in the scientific research community [1, 2]. The position of the defect levels significantly influences the photons of various absorption and emission energies, and the intensity of intrinsic magnetism is also affected by the number of unpaired electron spins created by the defect levels in MOS compounds [3]. Therefore, tuning the magnetic properties of the MOS nanoparticles by defect engineering could be directly correlated with the optical as-well-as photocatalytic properties [1, 2]. The tuning of the absorption spectra by the defects of varying charge states helps prepare light-emitting diodes, optic-magnetic-based devices, or optically writable oxides by the d^0-magnetism various wavelengths of light [4, 5]. The nature of MOS and their recent research on n-type and p-type models were remarkable in many applications [6].

The MOS nanoparticles with a unique combination of magnetic and charge transport properties such as TiO_2, ZnO, and SnO_2 are attracting substantial attention from the academic and industrial community. From all these various MOS materials, TiO_2 gains special attention due to its solid photocatalytic behavior and several other advantages like low cost, chemical and thermal stability, innocuity, and high refractive index [7, 8]. However, this wide-bandgap TiO_2 semiconductor is activated to perform photocatalysis only under irradiation of ultraviolet (UV) light, which needs to improve for practical applications. Many investigations have been reported and strategies to enhance TiO_2 photo-absorption capability [9–13]. Various strategies to improve photo-absorption, doping, co-doing, surface grafting, the combination of surface grafting and doping are efficient and established routes [14–18]. Suppose MOS nanoparticles are sitting in the core. In that case, the structure of MOS composite nanomaterials could be divided into four forms: core-shell, matrix-dispersed, Janus, and shell-core-shell structures, as shown in **Figure 1**.

For example, metal-doped TiO_2 nanoparticles improve the bandgap from the range of wide to mid-level electronic states, which imparts enhancement in charge migration or produces a strong redshift in the photo-absorption spectrum. More

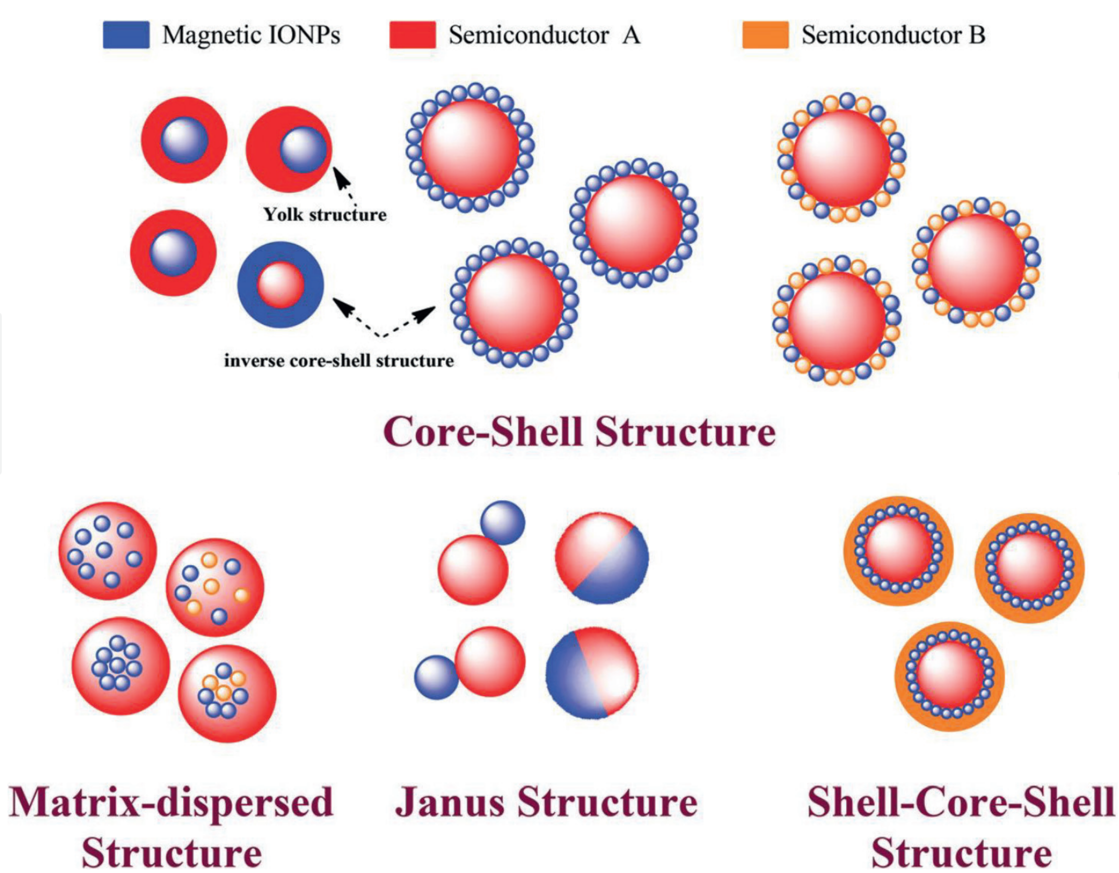

Figure 1.
Various structures of magnetic MOS composite materials. Blue spheres indicate the magnetic MOS nanoparticles, and the non-magnetic matrix and secondary materials are shown in another color [19].

emphasis has been explained in recent years on the [$Sn_xTi_{1-x}O_2$] system by coupling TiO_2 with SnO_2 oxide. It is highly acceptable that these new nanocomposites exhibit high photocatalytic activity compared to pure TiO_2 [20]. The simple hydrothermal synthesis route will produce SnO_2-TiO_2 nanocomposites; however, a small variation in the synthesis condition could lead to the formation of distinct secondary phases [21]. Cao *et al*. reported that annealing temperature strongly influences the Sn^{4+} ions doping into TiO_2 lattice, depends on temperature, which may substitute in lattice and exist as secondary phases like $SnCl_x$ or SnO_2 [22]. Sn-doped TiO_2 nanoparticles showed significant enhancement in performance as components of active visible light photocatalyst [23, 24], lithium-ion batteries [25], antibacterial activity [26], dye-sensitized solar cells [27], photo-electrochemical conversion [28] and water splitting [29] has been reported. It is important to find a reliable way to synthesize Sn-doped TiO_2 nanostructures, as TiO_2 and SnO_2 are environmentally benign, highly stable, and strong oxide materials [30, 31]. We developed a simple hydrothermal method to synthesize Sn-TiO_2 nanocrystals with sufficient oxygen vacancies, in this nanocrystal with different concentrations of Sn observed ferromagnetism and excellent photocatalytic activity [32, 33]. Wang *et al.* reported that Sn doping and Sn-Fe co-doping in TiO_2 showed a strong red-shift in the optical absorption spectrum [34]. The reason for this shift in absorption spectrum in the Sn-doped TiO_2 system comes from the most of the Sn 5 s states are located at the bottom of the conduction band where Ti 3d states are present and mixed with them.

The combination of non-transition metal and non-metal co-doping improves the visible-light activities of MOS materials. The non-metal doping in TiO_2 can make the new extra valance band and non-transition metal doping create the additional charge carrier traps, which improve the separation efficiency of photo-generated electron–hole pairs, reducing the bandgap width, and broadening the photo-absorption limit [35, 36]. Therefore, the combination of metal and non-metal co-doping will be applied to drastically enhance the visible-light photocatalytic performance of TiO_2. Among the various non-metals, nitrogen is an effective and promising candidate because N doping modifies the charge transport properties of TiO_2 along with which also induces the oxygen-defect sites, therefore improving the photocatalytic performance [37]. The substitutional nitrogen doping on TiO_2 showed an effective reduction in the bandgap width [38]. The nitrogen atoms were successfully substituted by either titanium or oxygen vacant atomic sites in the lattice of TiO_2 lattice. Asahi *et al*. reported that nitrogen atoms successfully replaced the oxygen lattice sites and reduced the bandgap width by mixing N 2*p* and O 2*p* states [39]. Wang *et al*. have studied that the TiO_2 nanocrystals were compacted closely together to form the solid TiO_2. By doping nitrogen, some extra impurity levels were distributed on the surface of the TiO_2 [40], as shown in **Figure 2a**. The solid TiO_2 with a close packing structure creates the difficulty of nitrogen doping into the bulk structure of TiO_2 and makes the diffusion of nitrogen difficult. However, the addition of the dodecyl tri-methyl ammonium bromide (CTAB) to TiO_2 nanocrystals produces a loose packing mesoporous structure, which is conducive for TiO_2 to take up ammonia into the interspaces.

Compared to undoped mesoporous TiO_2, the nitrogen-doped mesoporous TiO_2 with uniform distribution from the inside out produced successive energy levels from the bulk to the surface (**Figure 2b**). This subsequent impurity energy-band level formed by nitrogen doping are located above the valence band and successfully reduces the bandgap of the mesoporous TiO_2, which is the primary attribution for the improved photocatalytic activity throughout the visible-light range. Zhuang *et al*. have reported that the facile sol–gel method prepared Sn and N co-doped TiO_2 (SNT)

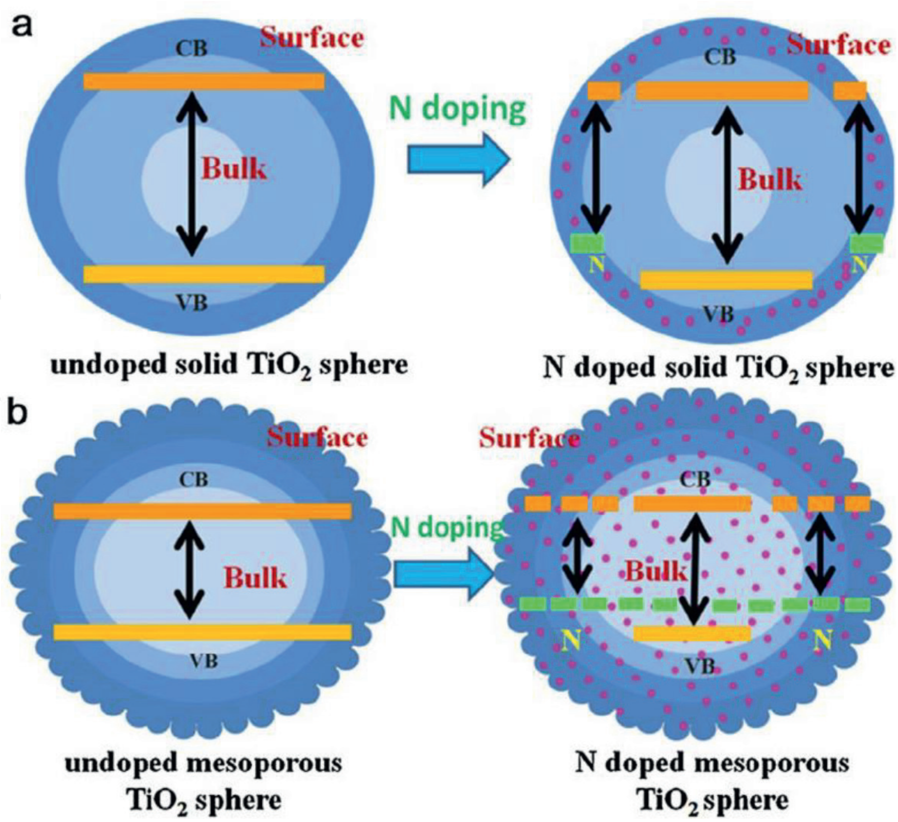

Figure 2.
Schematic diagrams depicting the band structures of (a) solid and (b) mesoporous TiO_2 before and after doping on N [41, 42].

photocatalysts. The post-nitridation treatment enhances the photocatalytic performance of co-doped TiO_2 under visible light or simulated solar light irradiation [43]. However, more studies are required to clearly understand the effect of doping on the physical, chemical and catalytic properties of SNT microspheres.

2. Diluted magnetic semiconductors

Diluted magnetic semiconductors (DMS), referred to as doping of magnetic impurities in bulk semiconductors, also called "semi-magnetic semiconductors", have been studied. This concept has had a particular interest in the research community for the past few years because ferromagnetism in diluted magnetic semiconductors (DMS) has been another important subject that can manipulate the carrier-associated charge and spin-based parameters [44, 45]. Especially, DMS with room temperature ferromagnetic oxides gained particular attention in the applications of magnetic fluids, biomedical, magnetic resonance imaging, catalysis, and environmental remediation [46, 47]. Wang *et al*. developed a facile method to synthesize ZnO crystals with Zn vacancies, and these doped Zn vacancies created p-type conductivity, room-temperature ferromagnetism, and excellent photocatalytic performance [48]. The recent development of ferromagnetic ordering in photo-induced transition metal-doped TiO_2 nanoparticles can be justified by creating defects in the samples [15]. However, the actual role of dopants (e.g. transition metals) at the room temperature ferromagnetism in TiO_2 nanoparticles is still an unclarified problem [49]. In one of our recent papers, our group proposed a new model for combined mechanics of ferromagnetism and their photocatalytic activity in wide-band-gap metal oxide-associated nanocomposites [32]. The study of ferromagnetism and photocatalytic activity on synthesized metal oxide-based nanocomposites suggesting a significant role of oxygen vacancies present on the surface and improved charge carrier concentration on magnetism and photocatalytic performance [50]. Charanpahari *et al*. reported room-temperature ferromagnetic nanocomposites showing better photocatalytic performance compared to commercially available diamagnetic photocatalysts under visible light irradiation [51]. Doping and co-doping have the advantage of high activity in semiconductor nanocomposites, which imparts the concept of magnetic photocatalysts with charge carrier and separation function was raised [51, 52]. Hence, in the research of photocatalytic activity today researchers are focusing on the development of photocatalyst possessing ferromagnetic property and visible-light activity.

DMS with room temperature ferromagnetism has been extensively studied for the applications of spin-based field-effect transistors, spin-based light-emitting diodes (LEDs), and non-volatile memory devices [53, 54]. In DMS materials are due to the coupling of magnetic ordering with one of the other types of ferroic ordering parameters like ferroelasticity or ferroelectricity, which are very interesting from the standpoint of device applications in fields such as spintronic and magneto-optics. Therefore, DMS offering certainly promising immense opportunities for new next-generation applications [55]. Theoretical and experimental studies on these metal oxides have shown improved ferromagnetism by the presence of defects or lightweight doping elements like C, N, and Li [56]. The addition of light elements in DMS can develop magnetism and significantly stabilizes the intrinsic defects in the oxide materials [56]. In these systems, the improved ferromagnetism is mainly attributed to the following mechanisms (i) the concentration of the oxygen vacancies (V_O) and defects sites and (ii) the substitution of an oxygen atom with the doping element and associated formation of spin-polarized states in the bandgap and (iii) the change of titanium oxidation state (Ti^{3+}) in the occurrence of ferromagnetic order. Therefore, defect engineering is a powerful tool to tune or improve the functional properties of the metal oxides like their electronic band structure, charge carrier transport, and catalytic performance [48]. The photocatalytic performance of TiO_2 significantly depends on their electrical and optical properties, which are primarily determined and altered by the crystal structure, optimized concentration of dopants, and defects [57].

Figure 3(**A**) showing the schematic diagram of the magnetic orientation of Fe doped TiO_2 nanoparticles, which are annealed under vacuum. It shows the possible paramagnetic species, their distribution in the nanoparticles lattice, surface, and interfacial boundary, and the potential interaction with ferromagnetic or antiferromagnetic species. The red circles inside the nanoparticles representing the magnetic polaron and overlapped magnetic polarons form BMPs. Along with BMPs, coupled F+ centres on the surface and interface also contribute towards ferromagnetism. However, F^{2+} without any electrons and F Centre with two trapped electrons are not likely to contribute towards ferromagnetism [58]. In vacuum annealed pristine TiO_2 nanoparticles, the total magnetization is contributed from the surface and interfacial oxygen vacancies, i.e. $M_{total} = M_{surface} + M_{interface}$. However, an extra BMP factor is added in the Fe doped vacuum annealed TiO_2 nanoparticles; therefore, the total magnetization is written as $M_{total} = M_{BMP} + M_{surface} + M_{interface}$. These observations of paramagnetic behavior in Fe doped TiO_2 nanoparticles suggest that the density of oxygen vacancies is possibly insufficient to generate solid ferromagnetic coupling with the nearest lattice site of Fe^{3+} ions. To improve the magnetization in pure and 2%

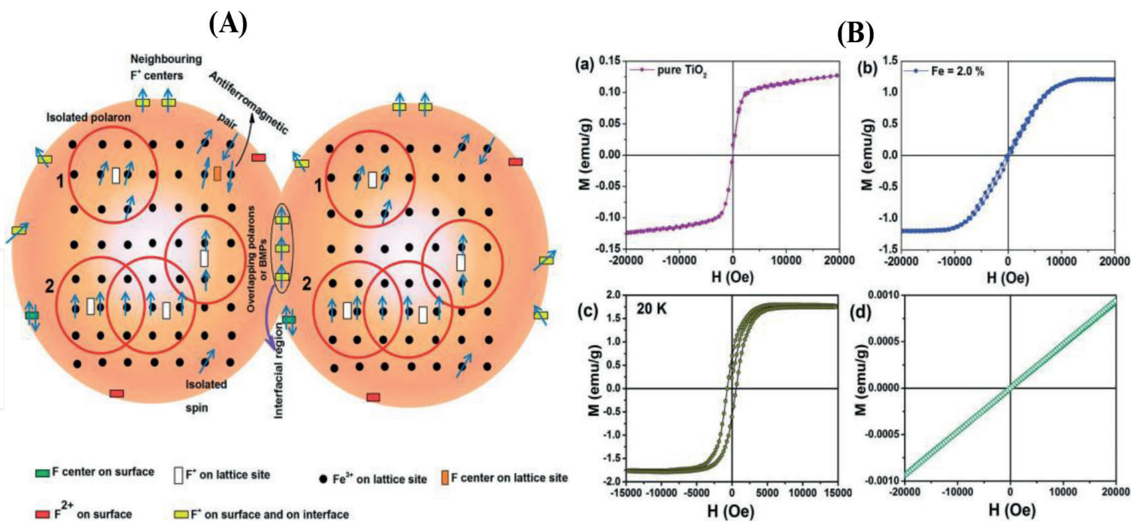

Figure 3.
(A) Diagram represents various possible magnetic species, their distribution, and interaction [58]. (B) M–H curves of vacuum annealed nanoparticles of (a) pristine TiO_2 and, (b) 2% Fe doped TiO_2 at room temperature, (c) 2% Fe doped TiO_2 at 20 K and, (d) paramagnetic M–H curve of vacuum annealed 2% Fe doped TiO_2 after reheating in the air at 450°C [58].

Fe doped TiO_2, vacuum annealed at 200°C for 3 h, generating donor carrier or oxygen vacancies. M–H measurements are carried out after the annealing on the samples, and as plotted in **Figure 3(B)**, initially diamagnetic pristine TiO_2 and paramagnetic Fe doped TiO_2 nanoparticles both have exhibited ferromagnetism. The observed ferromagnetism in pure TiO_2 nanoparticles could be attained from either Ti^{3+} ions or the presence of oxygen vacancies on the lattice site or the surface. Even though pristine and Fe doped TiO_2 showed ferromagnetically, the saturation magnetization of pure TiO_2 is less than that of Fe doped TiO_2 nanoparticles. The enhanced magnetization in Fe doped samples could be due to the extra magnetic interaction generated by both Fe dopants and defects in the ferromagnetic exchange coupling. The ferromagnetism is again switched back to paramagnetic for reheated vacuum annealed Fe doped TiO_2 in the air at 450°C samples as shown in **Figure 3(B)d**. The above results support that the oxygen vacancies possibly play the driving role in switching the magnetic ordering from paramagnetic to ferromagnetic and then back to paramagnetic in Fe doped TiO_2 nanoparticles. Just simple doping of Fe may not be sufficient to induce ferromagnetic solid exchange interaction. Only, when a high concentration of oxygen vacancies and Fe doping combining may participate in ferromagnetic exchange interaction.

Irradiation of various energy ion beams is one of the sophisticated techniques for incorporating the defects (i.e., vacancies, interstitials, etc.) into transition metal-doped metal oxide semiconductor matrix materials. Many researchers have studied that ion beam irradiation could improve the structural complexity of the ZnO nanoparticles by dissolving the secondary impurity phases, helps in substitutional incorporation of Mn^{2+} at the Zn^{2+} site (Mn and Zn) and improves the ferromagnetic property of the samples [59–61]. To avoid the segregation of nano-dimensional doped transition metal or its oxide clusters and to induce intrinsic structural defects in the host material in a controlled fashion, irradiation of a low energy ion beam using inert gases such as Xe or Ar is the best option which also eradicates the complexities arising from the chemical reactivity of the ion beams [60]. A multilayer coating and high-temperature calcination, thus affecting the photocatalytic efficiency, often influence the magnetic properties [62]. Therefore, a novel and facile approach to the low-cost preparation of the ferromagnetic and photocatalytic TiO_2 nanocomposite at relatively low temperatures is highly recommended. We have reported several research articles related to the photocatalytic performance and magnetic properties of TiO_2-based photocatalysts such as various metal (Sn, Cu and, Fe) oxide coupled TiO_2 [32], Sn doped TiO_2 [33], Fe_2O_3 coupled. Doped TiO_2 [63], nickel(II)-imidazole doped TiO_2 [64], hierarchical Sn and N co-doped TiO_2 [65] and hierarchical AgCl loaded Sn doped TiO_2 [66].

3. Visible light photocatalysts

Progressive research towards solar power-based energy conversion, wastewater treatment, and efficient photocatalysts attracting great attention [67–70]. Photocatalytic and photovoltaic solar cells convert solar-based light energy into chemical reaction and electrical power generation. Consequently, improving the stabilizations of photo-induced charge carrier transportation is the critical factor for light-harvesting systems. TiO_2-based materials are widely used in environmental and energy-related applications like photocatalysis, photovoltaics, artificial photosynthesis, and spintronic, which have been often foreseen. For better performance, TiO_2 is usually employed as nanocrystals or nanostructures [71–73]. However, the efficiency of photocatalytic activity of TiO_2 needs to improve to induce charge carrier activity using visible light or sunlight. Noble metal (Pt, Pd, Rh, and Au) doped and modified TiO_2 photocatalysts have been attracted great attention towards efficiency enhancement [74–76]. Especially in this context of an investigation, Ag-loaded TiO_2 that is Ag cluster-incorporated AgBr nanoparticles [77], Ag nanoparticles and CuO nanoclusters [78], and Ag/AgCl [79] in TiO_2 photocatalysts are undoubtedly intriguing to attain high performance [80]. The interfacial heterojunction between TiO_2 and SnO_2 particles can have a synergetic effect on photo activity [24]. Furthermore, any agglomeration in TiO_2/Ag/AgCl system due to the nature of the materials process used can influence the observed photocatalytic activity given that Ag/AgCl is a plasmonic system.

Therefore to improve the photocatalytic performance of metal oxide nanoparticles by expanding the range of photo-response and increasing the efficiency of electron–hole carrier separation, the hierarchical assembly of nanoscale building photocatalytic blocks with a tunable dimensionality and structural complexity offers a practical strategy towards the realization of multi-functionality of nanomaterials [81]. In general, hierarchical heterostructures are formed by connecting two different low-dimensional nanostructure materials; this type of structure provides the ultrahigh specific surface area and a network system consisting of parallel connective paths and provides interconnection of various functional components [82].

Liu et al., in their work, explained the photocatalytic mechanisms operating in the Fe(III)-$Fe_xTi_{1-x}O_2$ system as illustrated in **Figure 4**. are discussed [17, 18]. They are owing to the wide bandgap of pristine TiO_2, which is inactive under the illumination of visible or sunlight. However, by the selected surface grafting and bulk doping of Fe(III) ions, which have band energy levels identical to TiO_2, the visible-light absorption of TiO_2 is drastically improved by the bulk-doped Fe(III) ions. The QE was unaffected because of the efficient transfer of electrons between doped Fe(III) and surface Fe(III). Moreover, a good interface junction between surface-grafted and bulk-doped Fe(III) ions is needed for efficient charge carrier transfer. Notably, the visible-light activity reaction was markedly reduced by introducing a thin layer between the

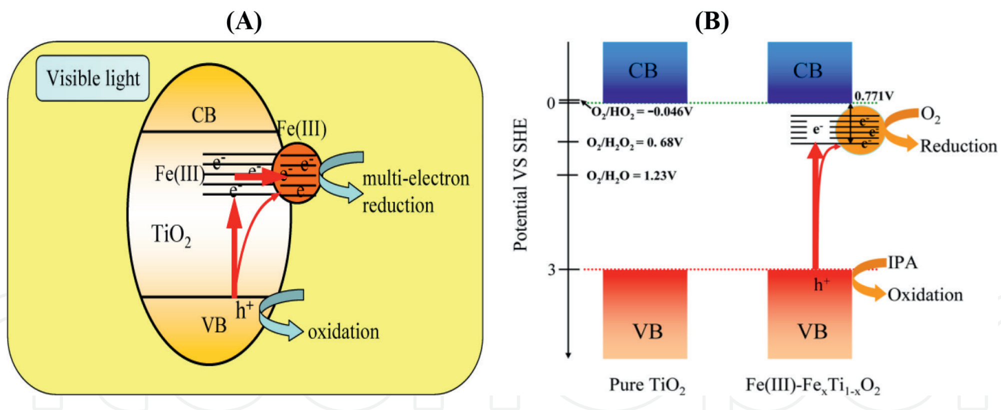

Figure 4.
(A) Proposed photocatalysis process. (B) Change in bandgap and photo-activity by Fe doping [17, 18].

surface Fe(III) ions and doped TiO_2. The photo-generated charge carriers are effectively transferred to the surface of Fe(III) doped TiO_2, which acts as an efficient co-catalyst for multi-electron reduction reactions. In photocatalysis by Fe(III) doped TiO_2, holes with high oxidation potential are kept in the deep level of the valance band and effectively decompose the organic compounds. Therefore, efficient visible-light photocatalysts with high R is achieved.

The conceptual ferromagnetic photocatalysts show a better charge carrier separation function to take advantage of high activity in the couple, doped, surface modified, or co-doped semiconductor nanocomposites. However, furthermore development in these TiO_2-based photocatalysts requires other strategies to improve photocatalytic efficiency. In today's research, one of the effective strategies is AgCl nanoparticles loaded in Sn-doped TiO_2 microsphere to enhance the visible-light activity have become an essential outcome in the photocatalytic and photovoltaic applications [83, 84].

4. Ferromagnetic TiO_2-based photocatalyst

In our previous reports, we worked on various concentrations of Sn doping to improve the structural, electronic, magnetic, and photocatalytic properties of TiO_2 nanoparticles [32, 33, 85, 86]. Significantly, the study of room temperature photocatalytic and ferromagnetic performance in the Sn-doped TiO_2 nanoparticles is one of the most emerging and fascinating fields in environmental remediation. Adding various concentrations of $SnCl_4$ in $Ti(NO_3)_4$ aqueous solutions produced any one of the anatase, a mixture of anatase-rutile and rutile phases of TiO_2 nanoparticles with the added Sn atoms, which are synthesized using the facile hydrothermal method. To study the photocatalytic performance of the synthesized Sn-TiO_2 nanoparticles, both methyl orange (MO) and *R*PhOH (where PhOH is phenol group and *R* is 3-NH_2, H, and 4-Cl) in water were chosen as model pollutants under both the illumination of visible light and UV light irradiation. Light irradiation showed a significant relationship between the Hammett substitution constant (σ) of RPhOH and the photocatalytic degradation efficiency of Sn-TiO_2 nanoparticles. The concentration of Sn doping significantly affected the structural, electronic, magnetic and, photocatalytic properties of the TiO_2 nanoparticles. Even after decade-long research, the actual mechanism of ferromagnetism combined with photocatalytic behavior in these materials is still not understood. However, hints about some of the critical factors that contribute to magnetism have been revealed. It is believed that oxygen vacancies, phase changes, and doping level play a significant role in the RTFM of semiconductor oxides; however, demonstration of a direct correlation between the magnetism, dopant concentration, oxygen vacancies, and photocatalytic activity has been strenuous. Because of these reasons, in this work, we made an effort to investigate the essential role of Sn^{4+} ions on the above properties of TiO_2 nanoparticles.

In another report, we first follow the facile hydrothermal synthesis route for preparing ST microspheres, followed by nitriding treatment by flowing an ammonia gas to successfully fabricate hierarchical SNT microspheres with V_O [64]. The fabricated as-prepared samples are characterized by the conventional analytical techniques and ^{119}Sn Mössbauer spectroscopy to understand the structure, magnetism, and photocatalytic performance. The main objective of this study is to improve the photocatalytic performance and RTFM of TiO_2 by the co-doping of Sn and N atoms. As compared to pristine and Sn doped TiO_2 nanoparticles, SNT microspheres showed significant absorption of visible light for photocatalytic activity is observed. Then we have further studied the photocatalytic movement of Rhodamine B (RhB) degradation under the illumination of visible light irradiation on pristine TiO_2, P25, ST, and SNT microspheres and observed vigorous photocatalytic activity in SNT microspheres. However, until now, no one reported magnetic studies on the SNT microspheres. Suppose, if the photocatalysts exhibit RTFM, the phenomenon may insist on the electrons trapped in V_O or structural defects. In this aspect, we can believe that this study can be implemented in the various other types of facile designing semiconductors to obtain an insight into the role of the visible light photocatalytic performance, RTFM behavior, and combined performance enhancement. In addition, we also studied the photovoltaic performance of ST and SNT microspheres in the applications of Perovskite solar cells. The combined mental and non-metal doped TiO_2 nanoparticles with other structural defect sites represent a new kind of semiconductor materials and provide novel opportunities for TiO_2-based materials.

For the first time, we have reported a facile hydrothermal synthesis route to successfully fabricate hierarchical AgCl in Sn-TiO_2 (AST) microspheres using post-calcination treated with different temperature samples [66, 87]. The primary objective of this study is to modify Sn doped TiO_2 by loading AgCl nanoparticles to enhance photocatalytic performance. Improved visible light absorption capability was observed in the AST microspheres compared to Sn-TiO_2, AgCl, Ag/AgCl, and commercial Degussa P25 photocatalysts. To check the photocatalytic performance of the as-synthesized AST microspheres, the rhodamine B (RhB) and 3-nitrophenol aqueous solutions were used as the model systems under visible light ($\lambda \geq 420$ nm). The obtained results indicate that the hierarchical AST microsphere photocatalysts showed a higher photodegradation rate than Ag/AgCl, AgCl, Sn-TiO_2, and the commercial TiO_2 (P25) materials. However, the study on various concentrations of AgCl in the AST microsphere is crucial to understand the optimized amount needed to obtain the best photocatalytic performance. To the best of our knowledge, for the first time, we reported the facile preparation route, high visible-light photocatalytic performance in hierarchical AST microspheres, and the magnetic behavior of these photocatalysts characterized by the ^{119}Sn Mössbauer technique. The new semiconductor family of noble metal halide and metal-doped TiO_2 nanoparticles opens up novel opportunities for TiO_2-based materials.

We have option $[Fe(III)(bipy)_2Cl_2)]^+[Fe(III)Cl_4]^-$ ionic salt-like complex as precursor complex [73]. The aqueous solution of precursor complex could behave like electrolytes. While the reduction potential from free Fe(III) to free Fe(II) is 0.77 V, that of photo-reduction from $[Fe^{III}Cl_4]^-$ to $[Fe^{II}Cl_3]^-$ is 0.34 V which indicates that photo-reduction of the $[FeCl_4]^-$ ion is easier than the normal chemical reduction of free ferric ions [12]. Hence chosen iron(III) complex interacts with n-type TiO_2 semiconductors.

It reduces Fe(III) to Fe(II) *via* interfacial electron transfer dynamics under dark (poor efficiency), near-UV (good efficiency), and visible light (moderate efficiency) irradiation systems. At the same time, the precursor complex is adsorbed on the TiO_2 surface to form a surface complex; it acts as a co-catalyst for the reduction of Fe(III) to Fe(II) with TiO_2. However, there are no reports on the study of photosensitized *via* IFET dynamics between Fe(III)-bipy complex (bipy without -OH or -COOH groups) and titania semiconductor interface until now. Hence, we report the near-UV and visible-light-induced IFET process on $[Fe^{III}(bipy)_2Cl_2][Fe^{III}Cl_4]$ (precursor complex) with TiO_2 NPs, and the photochemical product was mainly characterized by electronic absorption, Fe K-edge X-ray absorption fine structure (XAFS), electron paramagnetic resonance (EPR) and ^{57}Fe Mössbauer spectroscopes method. In addition, electron transfer was confirmed by cyclic voltammetric and photoluminescence measurements. However, the following factors control the IFET reaction, those are (i) the presence of TiO_2 nanoparticles, (ii) the irradiation time-lapse, (iii) light source with various wavelengths ($380 \leq \lambda \leq 520$ nm), and (iv) different types of TiO_2 nanoparticles.

In one of our works, nickel(II)-imidazole-anatase nanocomposites prepared by a simple adsorption method showed room-temperature ferromagnetism and good photocatalytic performance, which were designed by mixing of $[Ni(1\text{-}MeIm)_6]Cl_2H_2O$ complex and anatase TiO_2 starting materials in an aqueous medium [64]. Various conventional techniques as adsorption already elucidated the deposition of the surface species. We observed the ferromagnetic behavior in the composite sample under the vibrating sample magnetometer at room temperature. This Ni-dopedTiO_2 nanocomposite has good visible light absorption ability than pristine TiO_2. To understand and evaluate the adsorption and photocatalytic activity of the Ni-doped TiO_2 nanocomposite, selected methylene blue (MB) as an organic pollutant illuminating under visible light irradiation. We first reported the Ni(II)-imidazole complex deposited on the anatase (TiO_2) semiconductor with good photocatalytic and magnetic properties prepared by a simple adsorption method. The research of metal oxide-based photocatalysis is expected to open up a general method for synthesizing other transition metal-loaded metal oxide semiconductor photocatalysts.

In all of our previous reports covers the studies related to Mössbauer spectroscopic, photocatalytic and magnetic investigations of Sn and Fe doped TiO_2 nanocomposites [32, 33, 63–66, 73, 85–87]. Using the facile hydrothermal synthesizing route, we prepared Sn-based TiO_2. For structural and magnetic characterization, Mössbauer spectroscopy has unique advantages to mature into one of the classical techniques for Sn or Fe-based TiO_2 nanoparticles. Mössbauer spectroscopic results provided a strong understanding and evidence of the relationship between the structural, photocatalytic, and magnetic properties of Sn or Fe-based TiO_2 nanoparticles. The Sn or Fe-doped TiO_2 nanocomposites have promising applications in photocatalysis for water purification by degrading organic pollutants using efficient visible light absorption to produce strong stability and high photocatalytic activity. This review helps in the fundamental understanding of structural and magnetic properties of Sn or Fe-doped TiO_2 nanocomposites and their contribution towards environmental remediation by visible-light photocatalysis.

5. Conclusion

This review mainly highlighted the importance of the development of wide bandgap metal oxide nanoparticles for photocatalyst applications. Several researchers are primarily focused on developing a room-temperature ferromagnetic TiO_2 as the photocatalyst, which has a high potentiality to absorb visible light from the solar spectrum. However, there are certain limitations in pristine TiO_2 nanoparticles: their high photo-generated holes and electrons recombination rate, and they require UV light for photocatalysis. These problems can be overcome by introducing metallic or non-metallic dopants or creating oxygen vacancies and defect sites into TiO_2. The two successful approaches that have been discussed are the doping and grafting of TiO_2 nanoparticles with either anionic or cationic elements and coupling TiO_2 nanoparticles with other semiconductors. Further study is needed to understand the use of novel ferromagnetic metal oxide-based photocatalyst for large-scale applications.

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