Ferroelectric nanostructured oxides for solar fuel generation

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ABSTRACT
Decarbonising and cleaner economic growth through green, secure, and affordable future energy resources are among the highest priorities of our time. Market deployment for photocatalytic/electrochemical systems that convert solar energy to chemical fuels such as hydrogen has not yet been achieved. There has been intense work on methods of increasing output via reducing the rate of recombination and spatially separating reaction products through use of internal electric fields. One such method explored is use of ferroelectric polarisation. Of particular interest are composite nanostructures of ferroelectric ceramics that can prohibit bulk and surface recombination pathways providing significant improvements in overall solar to fuel conversion efficiency. This work presents the current understanding of mechanisms by which ferroelectric polarisation impacts solar fuel.

Introduction
It has been made increasingly clear in recent years that human consumption of fossil fuels is having a significant adverse impact on the environment. This has led to a global effort in reducing the reliance on fossil fuels and find new, clean, and sustainable sources of energy. Solar energy has been harvested on a commercial scale for many years through photovoltaic systems. However, similar market deployment for photocatalysis and solar fuels has not yet been achieved. Photocatalytic and photoelectrochemical systems can harvest solar energy through photogenerated charge carriers which take part in redox reactions to generate fuels such as hydrogen. The ability to convert solar energy into a fuel that can be stored as opposed to direct conversion to electrical energy is key for solar to become a reliable energy source. According to the 2019 Hydrogen Roadmap Europe, hydrogen energy demand in Europe could reach up to 665 TWh or by 2030, accounting for 6% of total energy demand. By 2050 hydrogen energy demand is projected to be as high as 2251 TWh corresponding to 24% of total demand [1].

The production of solar fuels has been considered as a potential alternative to fossil fuels since Fujishima and Honda discovered water-splitting in the 1970s [2]. However, despite significant progress in the development of photocatalytic systems many suffer from low energy conversion efficiency in the generation of solar fuels. In comparison, hydrogen generation technologies by electrolysis where the source of electricity is a renewable source such as photovoltaic cells or wind have been successfully deployed at a commercial scale. For example, commercially available photovoltaic modules in conjunction with an alkaline electrolyser have shown to produce as much as 1.129 mol·H₂·h⁻¹ [3]. Although at an earlier stage of development, photocatalytic and photoelectrochemical electrolysis eliminates the need for an electrolyser reducing complexity. Furthermore, the amount of electrical energy required is less due to the absorption of solar energy driving the electrolysis process [4].

Some of the main barriers to high performance photocatalysts are the recombination of photogenerated charge carriers and the backward reactions between reaction products. The recombination of charge carriers can be mitigated by the use of an internal electric field in photocatalysts [5–9]. Internal electric fields originate from p-n junctions, polar surface terminations, polymorph junctions and ferroelectric polarisation [10–12]. It can drive photogenerated charge carriers in opposite directions improving the charge separation efficiency and reducing the rate of recombination [13]. Additionally, the separation of the charge carriers can result in spatial separation of reduction and oxidation sites, therefore reducing the rate of backward reactions [14].

In recent years new materials, processing methods, and improved understanding of photocatalytic processes have resulted in significant progress in developing visible light photocatalytic systems [12,15]. Renewed interest in the field coincides with advances in areas such as hydrothermal and thin film processing which provide unprecedented quality and control at the nanoscale [16,17]. This has led to the development of...
new single and heterostructure systems with complex morphologies and high crystallinity. The dependencies of band positioning and ferroelectric properties upon nanostructure are known to be significant though not fully understood [18]. The ability to control band structure through nanostructure design could therefore be the key to a highly efficient photocatalyst for solar fuels (Figure 1).

**Photocatalysis mechanisms of ferroelectric materials**

Ferroelectric materials are characterised by their non-centrosymmetric structure, in which the positive and negative charges have different symmetry centres. This leads to electric polarisation in the absence of applied electric field, *i.e.* spontaneous polarisation, $P_s$. There are at least two equilibrium orientations of the spontaneous polarisation vector for ferroelectric materials. The vector can be switched between those orientations upon the application of an external electric field [19].

Many ferroelectric materials are metal oxides with the general formula, ABO$_3$, and perovskite structure, such as BaTiO$_3$ and PbTiO$_3$. The A-site cation is usually larger and primarily acts to stabilise the oxygen octahedra. The B-site cation is usually a small transition metal which occupies the centre of the oxygen octahedral. Figure 2 shows the crystal structure of BaTiO$_3$ at room temperature and the temperature above its Curie point, $T_C$. The distortion of octahedral oxygen and the shift of the B-site cation (Ti$^{4+}$) to off-centre positions give rise to a tetragonal structure at room temperature, which induces spontaneous polarisation in the crystal. At high temperature (> $T_C$) the crystal possesses a cubic structure, and thus no spontaneous polarisation exists.

Spontaneous polarisation will induce bound charges at the surface of ferroelectrics. These bound charge are compensated by free charge carriers and defects in the bulk (internal screening) and/or by surface adsorption of charged molecules from the environment (external screening) [19,21]. Figure 3(a) illustrates both external and internal screening mechanisms of ferroelectrics. For the domain with positive polarity (i.e, the positive end of the dipole is pointing towards the surface), the positive bound charges on the surface are screened by absorption of negative ions from the air and/or free electrons or negatively ionised acceptors or defects in the bulk. Conversely, for the domain with negative polarity, the negative bound charges are screened by adsorption of positive ions and free holes or positively ionised donors or defects.

The internal screening makes charge carriers redistribute near the surface of ferroelectrics, which leads to band bending and the formation of a space charge region. The direction of the band bending is controlled by the polarity of surface bound charges, as shown in Figure 3(b). On a surface with negative polarity, photo-generated electrons are repelled from the surface and move towards the bulk. Holes are enriched at the surface, resulting in a space charge region with upward band bending. While, on a surface with positive polarity, electrons are accumulated for screening, and thus cause the downward band bending. Consequently, reduction occurs on the surface of the positive domain and oxidation occurs on the surface of the negative domain. In other words, the internal field
created within ferroelectrics promotes not only the separation of photogenerated charge carriers, but also spatially selective oxidation and reduction [14]. Therefore, the recombination of charge carriers and intermediate species can be significantly reduced.

Often the polar bound charges cannot be completely compensated by internal screening. Therefore a strong Stern layer of chemisorbed molecules will be formed to externally screen the bound charges [23]. In other words, polarisation can enhance adsorption of charged molecules in the solution by forming a Stern layer [14]. The dipole moment of a polar molecule can interact with the polarisation of ferroelectric domains at the surface to reduce the energy required to break bonds. As a result, the photochemical activity can be enhanced [24–26].

Morris et al. reported that the internal field in ferroelectric materials can significantly extend charge carrier lifetimes, resulting in a $10^4$-increase compared to the non-ferroelectric materials [27]. The effect of ferroelectric polarisation on the spatial separation of reaction sites can be experimentally demonstrated by observing the distribution of reduction and oxidation products. As the effects of bulk and interfacial charge separation are highly directional, ferroelectric domain orientation is often used to analyse the impact of polarisation. Giocondi et al. demonstrated that the reduction of $\text{Ag}^+$ and the oxidation of $\text{Pb}^{2+}$ occurred preferentially at the positive and negative $\text{BaTiO}_3$ domain surfaces, respectively [28]. The reactions occurring on different domains can be described by:

$$\text{Ag}^+ + e^- = \text{Ag}$$

$$\text{Pb}^{2+} + 2\text{H}_2\text{O} + 2h^+ = \text{PbO}_2 + 4\text{H}^+$$

The impact of domain orientation on spatial separation of redox sites is illustrated well in Figure 4. The distribution of photochemical reaction products on ferroelectric surfaces is spatially localised, indicating that electrons and holes are spatially separated in the bulk.

**Ferroelectric perovskite oxides**

**Lead-based oxides**

$\text{PbTiO}_3$ has a band gap of 2.75 eV with suitable band edge potentials for water splitting. This arises from Pb 6s orbitals mixing with O 2p orbitals reducing the band gap while maintaining a band position below that of water oxidation [29]. Visible light photoactivity coupled with good water stability makes $\text{PbTiO}_3$ an ideal candidate for solar fuel generation. For example, Arney et al. prepared $\text{PbTiO}_3$ particles by using molten-salt flux methods with either $\text{PbO}$ or NaCl as salt flux. Homogeneous microstructures with more terraced surface features and edges were observed in the $\text{PbO}$ flux-prepared particles. But the NaCl flux-prepared particles were roughly spherical with few surface features. These powders were loaded with 1 wt-% Pt as cocatalyst before...
conducting a water-splitting test under visible light irradiation. Higher hydrogen and oxygen generation rates were observed in the PbO flux-prepared particles. The high activity is correlated with the formation of the surface with nano-features, which acts as preferential Pt deposition sites and assists electron/hole separation during the photocatalytic reaction [29]. Shabanalizadeh et al. synthesised PbTiO₃ nanoparticles with a size of 45–55 nm by the sol–gel method. After 60 min irradiation of UV light, the photodegradation of methyl orange solution was about 97%, which indicates good activity [30]. However, PbTiO₃ has not attracted so intense attention as other visible light semiconductors primarily due to toxicity issues associated with lead during the processing and application.

Lead Zirconate titanate (PZT) is one of the most widely used ferroelectric materials, its excellent piezo-electric properties have made it a popular choice for sensors and actuators. As with PbTiO₃, there has been little work concerning the photocatalytic performance of PZT due to its toxic nature. An investigation of photocatalytic hydrogen generation performance in Sr-doped PZT was carried out by Inoue et al. [31]. They conducted poling for PZT ceramic disc and evaluated photocatalytic activity by using the water-splitting test under UV light irradiation of polar surface of ceramic discs. The oxygen evolution was negligibly small for both polar surfaces. In contrast, the H₂ generation was 10 times higher for the positive than for the negative polar surface [31].

**BaTiO₃**

One of the earliest observations of a photovoltaic effect in a ferroelectric material is in a tetragonal BaTiO₃ crystal during the 1970s [32]. It can be viewed as a wide-bandgap semiconductor with a band gap value of 3.0–3.20 eV, requiring UV irradiation and limiting its solar-driven photocatalytic performance. However, BaTiO₃ offers a number of benefits over other potential ferroelectric photocatalysts. Its low cost, non-toxicity, and chemical inertness make it a popular choice for studies of the effects of ferroelectricity in photocatalysts [14,26,28]. Furthermore, BaTiO₃ has suitable conduction and valency band positions for water splitting under UV irradiation. Cui et al. demonstrated that the RhB degradation rate of tetragonal BaTiO₃ particles with submicron-size was 3 times higher than that of cubic counterpart although the cubic particles had much smaller particle size and consequently larger surface area. The enhanced activity in tetragonal BaTiO₃ particles clearly indicates the major contribution of ferroelectricity [14]. So far, like many metal oxides, BaTiO₃ suffers from low charge carrier mobility which has hampered its performance. Efforts have been made to improve performance using measures such as nanostructuring and doping. Chen et al. evaluated the hydrogen generation performance of room-temperature synthesised BaTiO₃ nanoparticles with an average size of 7 nm. Compared with commercial BaTiO₃ with the average size of 500 nm, nanoparticles showed 8 times higher photocatalytic hydrogen production rate (up to 143.8 μmol g⁻¹ h⁻¹) under UV light irradiation due to the combined effect of large specific surface area and ferroelectric polarisation [33]. Su et al. produced highly monodisperse BaTiO₃ nanoparticles with a size of 7.5 nm by using a hydrothermal reaction [34]. The decolourisation rate of Rhodamine B decreased about 12% when the temperature was increased from 30°C to 80°C. In contrast, when the large BaTiO₃ particles with a size of > 500 nm was used as photocatalyst, there was almost no change in decolourisation rate at the same temperature range of dye solution. Both Raman and piezoresponse force microscopy confirmed the existence of ferroelectricity in BaTiO₃ nanoparticles. However, ferroelectric polarisation gradually decreased with increasing temperature and nearly disappeared at 80°C, which caused the decreasing photocatalytic activity with temperature. But ferroelectric polarisation in large BaTiO₃ particles did not exhibit significant reduction from 30°C to 80°C. Hence, the large BaTiO₃ particles did not show temperature-dependent photocatalytic behaviour.

The doped element can act as a centre of visible-light absorption by making a donor or acceptor level, depending on dopants [35,36]. Rh has been demonstrated to be the most effective dopant since its incorporation into BaTiO₃ and can introduce donor levels within the band gap, and thus allows visible light absorption. Maeda studied the hydrogen generation performance of BaTiₜ₋ₓRhₓO₃ (for 0 ≤ x ≤ 0.05) using methanol as an electron donor [37]. They observed that the hydrogen generation rate increased with Rh content and reached a peak of 30.8 μmol h⁻¹ at x = 1 mol-% under visible light irradiation (λ > 420 nm). Performance subsequently dropped with further substitution up to 5 mol-% Rh. The increase in activity at x = 0–1.0 mol-% is attributed to the formation of new absorption bands in the visible light region. However, the excessive Rh doping worked as recombination centres between electrons and holes, resulting in reduced photocactivity.

**Alkali niobates**

Alkali niobates (LiNbO₃, NaNbO₃, KNbO₃) have been well reported as displaying good photocatalytic performance under UV irradiation. Their wide bandgap (> 3 eV) is due to their highly negative Nb 4d conduction band edge potential. However, doping can reduce the band gap and make them photoactive under visible light. Yu et al. produced carbon-doped KNbO₃ photocatalyst via a combination of hydrothermal and post-calcination processes. Compared with undoped
KNbO₃, the carbon-doped KNbO₃ displayed 42 times increase in H₂ generation from a methanol solution under simulated solar light [38]. The carbon doping would generate oxygen vacancies in KNbO₃, which act as the shallow traps to capture the photogenerated electrons, and thus retard the recombination of charge carriers and enhance photocatalytic activity.

The composition of K₀.₅Na₀.₅NbO₃ solid solutions, as a lead-free alternative to PZT for ferroelectric applications, is close to the morphotropic phase boundary (MPB) between two orthorhombic phases, thereby resulting in good ferroelectric properties and large electromechanical coupling coefficients [39]. Park et al. produced K₀.₅Na₀.₅NbO₃ solid solution powder by solid state reaction. They conducted a corona poling process in order to generate an enhanced polari
dation in the powder. The H₂ evolution rate of the poled powder from a methanol solution increased by up to a factor of 7.4 compared with the non-polied KNN powder [40].

**BiFeO₃**

In the field of photocatalysis, there have been few materials studied as intensely as BiFeO₃ in recent years. It has a rhombohedral structure at room temperature which is distorted as by Bi lone pairs. It exhibits multiferroic behaviour, i.e. a coexistence of ferroelectric and magnetic order. The spontaneous polarisation of BiFeO₃ is as high as 100 μC cm⁻² [41]. Unlike many oxides, rhombohedral BiFeO₃ is well suited to visible light absorption due to its direct bandgap of ~2.67 eV [42]. In addition, it benefits from being non-toxic and relatively low cost. However, despite its visible light band gap and ferroelectric behaviour, BiFeO₃ suffers from low photocatalytic performance. This is caused primarily by low charge carrier mobility resulting in rapid recombination and has so far prevented it from becoming commercialised. Furthermore, there are few studies of BiFeO₃ alone that consider hydrogen evolution and CO₂ reduction, with the majority focusing on the degradation of organic dyes. Nevertheless, such studies have provided insight into the impact of dopants on factors such as absorption, recombination, and band structure [13,43,44].

The processing methods and conditions are crucial to the performance of all photocatalysts. BiFeO₃ is particularly sensitive to processing methods. In BiFeO₃ produced by solid-state reaction, impurity phases Bi₂Fe₂O₉ and Bi₂₅Fe₄O₉₀ are often formed due to the poor stability of BiFeO₃ at high temperature [45]. These impurity phases are detrimental to the ferroelectric properties and charge transport, and thus have stimulated work on alternative methods for processing BiFeO₃, particularly in cost-effective low-temperature synthesis routes [46–49]. Deng et al. used a PVA-based sol–gel method to produce pure BiFeO₃ nanoparticles with a size of 50–60 nm for hydrogen generation [50]. Hydrogen generation was assessed under solar simulated light and compared with commercially produced P25 TiO₂. The results showed hydrogen generated by the BiFeO₃ nanoparticles was three times that of P25. The improved photocatalytic activity of BiFeO₃ over TiO₂ nanoparticles was attributed to both the visible light absorption and efficient charge separation in BiFeO₃. However, the cost of this method would likely be an issue for commercialisation because of the annealing process at 600°C for 2 h in a N₂ atmosphere was employed.

More recently a hydrothermal synthesis route has been used to produce BiFeO₃ nanoparticles for hydrogen generation [51]. The BiFeO₃ nanoparticles synthesised at reaction temperatures between 160°C and 200°C showed good crystallinity without impurity phases. The BiFeO₃ powder produced by both hydrothermal reaction and solid-state reaction were compared in their hydrogen generation performance. The BiFeO₃ nanoparticles produced by hydrothermal reaction could generate more than two times of hydrogen via water splitting than that of powder produced by the solid state reaction as well as commercially available Degussa P25 TiO₂. The improved photocatalytic activities of BiFeO₃ nanoparticles were ascribed to their high crystallinity, high phase purity, excellent morphology, higher specific area, and efficient charge carrier separation and migration.

Although BiFeO₃ exhibits photoactivity under visible-light irradiation and conduction and valency bands overlap hydrogen evolution (HER) and oxygen evolution (OER) reaction potentials respectively, there has been little success of water splitting with under visible light. BiFeO₃ has been demonstrated as effective at visible light water oxidation [52,53], the low conduction band edge limits the HER. Although HER has been observed with reduction from higher energy states within the conduction band, this narrows the range of the solar spectrum that can be utilised [51]. The incorporation of rare earth metals is thought to be an effective method to improve visible light absorption as well as improving charge separation [54]. Yang et al. studied the effect of isovalent A-site doping of Gd³⁺ for Bi³⁺ on hydrogen generation, albeit from a methanol solution [55]. The doping of the smaller Gd³⁺ ions led to a decreased lattice parameter. But the effect of doping on ferroelectric properties was not reported. The measurement of photocurrent intensity for both undoped and Gd doped BiFeO₃ indicates that doping effectively separate charge carriers and extend their lifetime. The observed 3-fold increase in hydrogen generation, from 21.9 to 67.6 μmol cm⁻² h⁻¹, was attributed primarily to a reduction in the band gap due to doping and resulting greater absorption capability. The impact of the increase in bulk oxygen vacancies on visible light adsorption was addressed however the impact on charge separation was not discussed [56]. A
more complete review of the effects of dopants on photocatalytic performance can be found elsewhere [57].

There are more reports about using BiFeO3 for photocatalytic degradation of organic pollutants in water [58]. Gao et al. produced BiFeO3 nanoparticles with the size ranging from 80 to 120 nm by the sol–gel method [59]. They also synthesised bulky BiFeO3 powder by the rapid liquid phase sintering technique. Although both bulk and nanoparticles were able to decompose methyl orange under UV-vis light irradiation, the degradation rate with nanoparticles was significantly higher than that of bulk counterpart due to the higher surface area of nanosized particles. More interestingly, nanoparticles exhibited tremendously degradation capability under visible light irradiation due to their small band gap ($E_g = 2.18$ ev). Chen et al. produced defective BiFeO3 nanocrystals by hydrothermal method followed with annealing at 180°C with hydrogen at a pressure of 2 MPa [60]. Oxygen vacancies were introduced on the surfaces of BiFeO3 nanocrystals during the hydrogenation process. The formation of surface oxygen vacancies not only reduced band gap of BiFeO3 and enhanced light absorption capability, but also acted as the trapping centres for photogenerated electrons and promoted the separation of carriers. Thus, the hydrogenated BiFeO3 nanocrystals exhibited nearly four times methyl orange (MO) photodegradation efficiency higher than that without hydrogenation treatment under visible light irradiation. Hengky et al. synthesised BiFeO3 nanoparticles with sizes of 20–100 nm by using an auto-combustion technique [61]. Nanostructured BiFeO3 showed rapid 95% decolourisation of RhB dye solution under artificial natural sunlight illumination in 10 min at pH = 2. Whereas TiO2 showed 90% decolourisation of RhB in 30 min. This clearly indicates BiFeO3 is favourable over other semi-conductor systems in terms of RhB decolourisation efficiency. However, BFO produced using the auto-combustion technique is not photostable due to photocorrosion of the material during illumination. Huo et al. fabricated BiFeO3 hollow microspheres by using a solvothermal synthesis route [62]. Much higher methylene blue degradation rate under visible-light irradiation was observed for BiFeO3 hollow microspheres compared to TiO2. This is attributed to the high crystallisation, high surface area with hollow structure, narrow band gap, and effective charge carrier separation by ferroelectric polarisation. Additionally, there was no decrease in activity after recycling tests for five times, which indicates excellent stability of BiFeO3 microspheres produced by the hydrothermal method.

**Ferroelectric heterostructures**

Using a combination of materials in a heterostructure system can offer significant enhancements in performance. Such benefits can include improved charge transfer, reduced photo-corrosion, and increased solar absorption efficiency. This section focuses primarily on the influence of ferroelectric polarisation within different heterostructure architectures. A more general description of such systems can be found elsewhere [63].

**Reduction and oxidation co-catalysts**

It is common in photocatalysis studies for the surface of photocatalysts to be decorated with co-catalysts. These are based on noble metals such as in Pt and RuO2 where are effective reduction and oxidation co-catalysts respectively. These co-catalysts are trapping sites for charge carriers, providing interfacial charge separation and lower the activation energy required for redox reactions. The ability to lower the activation energy of redox reactions is of particular interest when considering OER in both water splitting and CO2 reduction [64]. As OER requires a large overpotential, photocatalytic efficiency is often low therefore electron donors such as methanol are frequently used. Furthermore, many of the noble metals used can induce surface plasmonic resonance (SPR), which can improve visible light absorption capabilities.

Cui et al. demonstrated how charge separation can be enhanced by co-catalyst loading on ferroelectric materials [14]. They considered the performance of Ag-loaded tetragonal BaTiO3 for photodegradation of rhodamine B. Their result showed that the ferroelectric tetragonal particles had the degradation rate 72-times higher than the non-ferroelectric cubic particles without Ag-loading. Furthermore, considering the impacts of ferroelectric polarisation and Ag-loading independently 3-fold and 8-fold improvements are observed respectively. These improvements appear modest in comparison to the combination of the two. It is therefore clear that optimisation is not caused by the two mechanisms acting independently but co-operatively. [65].

The use of rare and expensive noble metals for co-catalysts is obviously problematic for commercialisation of photocatalytic systems. As a result, there has been work recently to find more economical and earth abundant alternatives [64,66,67]. Therefore, the incorporation of carbon-based structures such as nanotubes (CNT) and nanosheets has attracted much attention due to the high conductivity and good stability. One material that has attracted much interest is reduced-graphene oxide (rGO). The combination of ferroelectric charge separation and excellent charge carrier transport in rGO has been explored by Jiang et al. [68]. BaTiO3 nanoparticles were loaded onto an rGO sheet (Figure 5(a)) to evaluate the performance in the degradation of various organic pollutants under visible light. Considering Figure 5(b), there is a 75% degradation of
Figure 5. (a) Schematic illustration of BaTiO\textsubscript{3} particles deposited in rGO sheet. (b) Photocatalytic degradation of MB under visible light for different GO concentrations used in the synthesis [68]. Reprinted with permission of Wiley from [68]. Copyright 2016.

MB in 20 min, with similar results seen in the degradation of MO and RhB. This was a 9-fold increase compared to pure BaTiO\textsubscript{3} nanoparticles. It was shown through photoluminescence that the rate of recombination was greatly reduced, which can be attributed in part to interfacial band bending at the BaTiO\textsubscript{3}-rGO interface [65]. The band gap was observed to decrease from 3.3 to 2.4 eV compared to pure BaTiO\textsubscript{3}, resulting in improved visible light absorption. This was attributed to the effect of Ti-O-C bonding at the rGO-BaTiO\textsubscript{3} interface, with unpaired C electrons resulting in the gap narrowing [69].

**Type II heterojunctions**

The use of two different photocatalytic materials to form heterostructures has been employed for many years as a means of improving photogenerated charge separation. Where conduction and valency band potentials of a photocatalyst are below those of another, when the two materials come into contact the differences in potential result in band bending at the interface (Figure 6(a, b)). As a result, there is spatial charge separation across the heterojunction. There have been a number of examples of how this charge separation mechanism can be further enhanced through ferroelectric polari- sation [11,65,70]. Where polarisation is matched to the interface, the space charge region between the photocatalysts has been shown to be extended, aiding charge transfer (Figure 6(c, d)).

There are many examples of such structures displaying improved photocatalytic activity over single material photocatalysts. Studies have focussed primarily on use of metal oxides such as BiVO\textsubscript{4}, Fe\textsubscript{2}O\textsubscript{3}, and TiO\textsubscript{2} among others [71–73]. Niu et al. observed the effect of loading \textit{p}-type CuO onto \textit{n}-type BiFeO\textsubscript{3} particulate photocatalysts [74]. An increase in photocatalytic activity of 3.3 times that of BiFeO\textsubscript{3} alone and 4.7 times that of CuO was observed when considering the degradation of methyl orange under visible light. This increase in activity is attributed to improved charge separation as a result of the formation of space charge regions at CuO-BiFeO\textsubscript{3} interfaces.

The transfer of electrons/holes to a lower/higher band potential prior to redox reactions can lead to a significant decrease in overpotential and prevent the reaction altogether. This issue is particularly important when considering OER, due to it being a 4-electron reaction and requiring greater energy to sever the O=O bond [75]. This has led to difficulty in developing type II heterostructures with suitable band structures to enable visible light water splitting or CO\textsubscript{2} reduction [76]. However, type II heterostructures can undeniably provide a simplistic method for effective enhancement of charge separation as well as broad-ening light absorption capability [77]. Innovations in such heterostructures will be discussed further when considering core–shell structures.
As discussed, it is difficult to find a single photocatalytic material with a visible light bandgap which also has suitable band positions for the required redox reactions. Additionally, it is also desirable to have a wide enough band gap to provide a significant overpotential to aid the reactions. Therefore, it is unlikely that any single material will be able to satisfy all these requirements. Attention has been drawn to multi-excitation systems to obtain large overpotentials using visible light absorption. This is achieved using narrow bandgaps semiconductors with off-set band structures, as shown in Figure 7(b). This allows for the recombination of photogenerated electrons from the conduction band in PS (photosystem) II and holes from the valency band of PS I. A mediator is often incorporated between photocatalysts to facilitate charge transfer. The electrons can then be photoexcited to the conduction band of PSI for the reduction reactions. Holes generated in the valency band of PS II participate in oxidation reactions. However, such systems have several factors which hinder photocatalytic performance. The most obvious being that due to the requirement for multiple excitations the energy conversion efficiency will obviously be limited. The efficiency will also be reduced by the energy needed for charge transport from PS II, to the mediator, to PSI [75,78].

Although Z-scheme systems are promising candidates for a water-splitting system, there has been difficulty in producing them with effective control of charge transfer between photocatalysts. Ferroelectric polarisation could be used to manipulate the band bending at interfaces by switching the direction of polarisation. Therefore, ferroelectric polarity could be used to manipulate interfacial band bending promoting directional charge transfer.

The impact of ferroelectric polarisation on Z-scheme charge transfer was first observed in a BiVO₄-BiFeO₃-CuInS₂ system for the degradation of organic pollutants [79]. It was found that the rate of 4-nitrophenol degradation was increased from 0.38 to 1.19 h⁻¹ with poling of the BiFeO₃ layer (Figure 8(a)) with a similar enhancement observed in the degradation of 2,4-dichlorophenol. Using electron scavengers, it was confirmed that the degradation enhancement arose from electron accumulation at CuInS₂, as shown in Figure 8(c). This provides further evidence of improvement of directional charge transfer in the system with polarisation.

The generation of solar fuels using Z-scheme systems is a popular topic. However, there has been little progress in enhancement through ferroelectric polarisation. There have been several examples of ferroelectric materials such as BiFeO₃ and BaTiO₃ being incorporated into Z-scheme systems [80,81]. These reports, however, often neglect to consider dipole orientation which is known to be crucial to the band bending effect at interfaces. Therefore, there will not necessarily be an enhancement of the charge transfer as a result of enhanced band bending at the interface.

Recently one of the most intensively studied materials in the field of photocatalytic solar fuel generation has been g-C₃N₄. This is due to its high stability, low cost as well as its favourable band structure. g-C₃N₄ has a bandgap of ~2.7 eV. Limitations however remain, with high recombination rates and electrical conductivity hindering the photocatalytic performance [82]. Therefore, ferroelectricity has been explored as a possible method of enhancing charge separation to harness the visible light response of g-C₃N₄.

Wu et al. deposited g-C₃N₄ and Au particles onto BaTiO₃ nanowires to produce a Z-scheme system for hydrogen generation [81]. They observed a hydrogen generation performance of 1769.3 μmol g⁻¹ h⁻¹ under solar irradiation, an 18-fold increase compared to g-C₃N₄ alone. This was attributed in part to ferroelectric polarisation aiding charge separation, though there is likely a contribution from the SPR effect in Au injecting electrons into the system. As both g-C₃N₄ and BaTiO₃ are n-type semiconductors in the absence of Au, they formed a type II heterojunction. In this case,
hydrogen generation is negligible due to the accumulation of electrons in the less negative BaTiO3 conduction band. Shephvand et al. observed water splitting in a g-C3N4/BiFeO3 system [83]. The hydrogen generation, even under UV light, was significantly lower than observed in a BaTiO3-based system by Wu et al. However, the lack of Au mediator would significantly reduce cost and therefore likely to be explored further.

Core–shell structures

Core–shell heterostructures usually consist of a ferroelectric microcrystalline core with a non-ferroelectric coating forming a nano-shell around it. The internal field originated from ferroelectric core can induce the separation of charge carriers and promote charge transport to the shell with a high surface area, resulting in increased photocatalytic activity. In addition, the shell serves as protection against photocorrosion and degradation in an aqueous environment for the ferroelectric core, resulting in excellent stability of the catalyst. Compared with other heterostructures, core–shell heterostructures offer more freedom in the catalyst design by using different functionalities of the core and shell with high surface area and favourable band edge locations to optimise solar light absorption. As a result, the core–shell hierarchical structure presents a novel strategy for enhanced reactivity of photocatalysts. The photocatalytic activity of such a core–shell photocatalyst depends on the photon absorption location, carrier diffusion length, and carrier interfacial transfer. If the interfacial transfer is significantly impeded or no light absorption occurs in the core, then the heterostructures will have similar or worse properties than the coatings themselves [84]. The impact of ferroelectric polarisation in such structures has been the subject of significant work in recent years as will be discussed.

Li et al. prepared heterostructured powders consisted of microcrystalline PbTiO3 cores coated with nanostructured TiO2 shells by a sol–gel method [85]. When the heterostructured powder was exposed to visible light ($\lambda > 420$ nm), the degradation rate of methylene blue solution was at least 4.8 times greater than either of the component phases alone or mechanical mixtures of the phases. The enhanced activity clearly indicates the role of the core–shell architecture and the interface between the two phases. Annealing at proper conditions can improve the crystallinity of the shell and structural integrity of the interface, which contributes to the improved activity. Li et al. prepared heterostructured photocatalysts with nanostructured TiO2 shells surrounding microcrystalline cores of (Ba,Sr)TiO3 for photochemical hydrogen production from water/methanol solutions.
The (Ba,Sr)TiO$_3$/TiO$_2$ core-shell photocatalysts exhibited the highest hydrogen production rates compared with those of freestanding TiO$_2$, (Ba,Sr)TiO$_3$ alone or mechanical mixtures of component phases. The improved reactivity of core-shell photocatalysts resulted from the efficient charge separation in the ferroelectric core, efficient transfer of charge carrier across the core/shell interface, and high surface area and reactivity of the nanostructured TiO$_2$ shell.

Subsequent work systematically evaluated the effectiveness of various ferrite and titanate-based perovskites with TiO$_2$ shell [86]. ATiO$_3$/TiO$_2$ (A = Pb, Fe) showed much higher photocatalytic activity under visible light irradiation than their components alone, while AFeO$_3$/TiO$_2$ (A = Bi, La, Y) did not. The enhanced activity of the titanates was considered to be due to the continuity of Ti–O–Ti bonds across the ATiO$_3$/TiO$_2$ interface, which might reduce the barrier for charge carrier transmission across the interface. Conversely, photogenerated charge carriers are more difficult to transport across the ferrite–titanate interface. This work provides insight for materials selection in composite catalyst design.

Cui et al. fabricated BaTiO$_3$/α-Fe$_2$O$_3$ core–shell photocatalysts with different concentrations of Fe$^{3+}$ precursor by the sol–gel method and studied decolourisation of rhodamine B of the above photocatalysts under simulated sunlight [72]. Although the increasing concentration of Fe$^{3+}$ precursor led to decreasing band gap values of BaTiO$_3$/α-Fe$_2$O$_3$ structure, the highest photocatalytic activity was achieved at the lowest concentration of Fe$^{3+}$ precursor. TEM observation revealed that the morphology of α-Fe$_2$O$_3$ shell changed from island to the thick layer with increasing concentration of Fe$^{3+}$ precursor. They proposed a morphology model to explain the effect of concentration of Fe$^{3+}$ precursor on photocatalytic behaviour, as presented in Figure 9. The island-like Fe$_2$O$_3$ on the surface of BaTiO$_3$ allows the photons to excite both Fe$_2$O$_3$ and BaTiO$_3$ (Figure 9(a)). There are numerous triple points between Fe$_2$O$_3$, BaTiO$_3$, and dye solutions. They provide active sites for redox reactions, thus facilitating dye degradation (Figure 9(b)). However, when the content of Fe$_2$O$_3$ is too high, the number of triple points is reduced and the continuous Fe$_2$O$_3$ layer is formed around BaTiO$_3$ particles. Such a Fe$_2$O$_3$ layer absorbs the majority of light, and thus weakens the photoexcitation of BaTiO$_3$ (Figure 9(c)). Moreover, the continuous Fe$_2$O$_3$ layer suppresses direct contact between dye solutions and electrons/holes in BaTiO$_3$, which also caused the reduced photocatalytic performance at higher Fe$_2$O$_3$ content. To elucidate the role, ferroelectric polarisation cubic and tetragonal BaTiO$_3$ cores were used. The ferroelectric, tetragonal, core displayed a 57% higher rhodamine B degradation rate under solar irradiation and 29% higher under visible light compared to cubic BaTiO$_3$ core. The contribution of ferroelectric polarisation to the band bending at the BaTiO$_3$–Fe$_2$O$_3$ interface could be the reason through improved charge separation.

![Figure 9](https://example.com/figure9.png)

**Figure 9.** Schematic showing the influence of existing morphology of Fe$_2$O$_3$: (a) the islandlike morphology allows irradiation light to excite both BaTiO$_3$ and Fe$_2$O$_3$; (b) triple points between the dye solution, Fe$_2$O$_3$, and BaTiO$_3$ provide active sites for redox reactions. Reprinted with permission from [72]. Copyright 2017, American Chemical Society.

Epitaxial growth in photocatalytic and photoelectrochemical systems

The use of epitaxial growth as a means for preparing heterostructure photocatalysts has attracted considerable interest, particularly for fabrication of photoelectrodes [87,88]. The ability to match the lattice between the substrate and film provides a high degree of control over parameters such as domain structure and orientation. This has been demonstrated by Yang et al. who successfully produced a monodomain BiFeO$_3$ film on the surface of a SrTiO$_3$ substrate with only one ferroelectric variant [89]. Large ferroelectric polarisations have been observed in epitaxy films, attributed to the strain induced by the substrate causing an increase in dipole moment. Studies have been collated and statistically analysed to determine the dependence of optical properties of epitaxy BiFeO$_3$ films on various parameters [42]. These show that the band gap is dependent upon film thickness and epitaxial strain, with the band gap found to decrease with increasing thickness. This is likely due to relaxation of strain changing in the tilt of the oxygen octahedra resulting in the reduction of Fe-O-Fe bond length and increase in the bond angle [46]. In turn, this will impact the bandgap due to the valency band consisting of overlapping Fe 3d and O 2p orbitals. The combination of high ferroelectric polarisation and tuneable bandgaps is a promising prospect for the development of high-efficiency photocatalysts [90]. In addition, epitaxy films have been observed to have fewer defects than those found in bulk polycrystalline structures and therefore fewer recombination sites [91,92].

The substrate plays an important role in the development of the films. The effects of different substrates on the structural and photocatalytic properties were demonstrated by Xu et al. by considering the impact on BiFeO$_3$ films on Pt/Ti/SiO$_2$/Si, FTO and
ITO substrates [93]. Similar results for absorption spectra and photodegradation of Congo red (CR) were observed in FTO and ITO. However, the Pt/Ti/SiO₂/Si displays significantly higher visible light absorption. This is the likely cause of the corresponding increase in photocatalytic performance, though performance appeared unremarkable with 16% degradation of CR in 4hrs. Nevertheless, the results highlight the significant impact of the substrate on the photoactivity of the film. The disparity in performance in this instance was attributed to the effect of grain size, with the finer grain structure enhancing visible light absorption [94].

As well as controlling the domain structure within films, polarisation in the substrate has also been shown to impact the location and morphology of epitaxial growth. Li et al. investigated the impact of ferroelectric polarisation in single-domain PbTiO₃ substrates on the epitaxial growth of TiO₂ [95]. They found that the growth of TiO₂ was highly tuneable with varying morphologies produced which can be seen in Figure 10.

![Figure 10](image1.png)

**Figure 10.** Illustration showing the tuneable morphology of epitaxial growth using ferroelectric polarisation. Reprinted from [95] with permission from Elsevier. Copyright 2018.

![Figure 11](image2.png)

**Figure 11.** (a) Potential distribution of TiO₂/5 nm BaTiO₃/NaOH heterojunction. (b) Potential distribution of the TiO₂/40 nm BaTiO₃/NaOH heterojunctions. (c) J–V curves of the unpoled, positively poled, and negatively poled TiO₂/5 nm BaTiO₃ NWs. (d) J–V curves of the unpoled, positively poled and negatively poled TiO₂/40 nm BaTiO₃ NWs [96]. Reprinted with permission from [96]. Copyright 2015. American Chemical Society.
The photocatalytic performance of the heterostructures showed a strong dependence on polarisation orientation. Samples with TiO₂ grown on the positive and negative only polar faces displayed superior degradation of full name of MB. On the other hand, samples with growth on the positive surface showed prior degradation of full name of MB. On the other hand, negative and negative only polar faces displayed superior photocatalytic performance.

Epitaxial growth methods have also been combined with core–shell systems. One such system used a nanowire-array photoanode consisting of a TiO₂ core with a BaTiO₃ epitaxial shell produced by a surface conversion process [96]. By considering the core–shell system in the form of a nanowire array it is possible to improve the conversion process [96]. By considering the core–shell interface extending the depletion region in the TiO₂ core (Figure 11(a, c)). With increasing thickness of the BaTiO₃ shell (< 40 nm), there was a notable reduction in the photocurrent generated. The higher performance in thinner shells was caused by holes, which were able to tunnel through the thin shell.

Table 1. Photocatalytic properties of some ferroelectric semiconductors.

| Material                  | Bandgap /eV | Structure     | Modification | Photocatalytic Performance | Experimental Conditions                                      | References |
|---------------------------|-------------|---------------|--------------|----------------------------|-------------------------------------------------------------|------------|
| BiFeO₃                    | 2.1         | Powder        | –            | \( k = 0.323 \text{ min}^{-1} \) Degradation of RhB under 500W Xe lamp with \( \lambda = 420 \text{ nm} \) cut-off, Hydrothermal synthesised powder | [51]       |
|                           | 2.17        | Powder        | Gd³⁺ doped   | \( 67.6 \mu \text{mol cm}^{-2} \text{ h}^{-1} \) H₂ generation from methanol solution under simulated sunlight | [55]       |
|                           | 2.06        | Powder        | La³⁺ doped   | \( k = 0.01996 \text{ min}^{-1} \) Degradation of phenol under simulated solar light, sol-gel synthesised | [43]       |
|                           | 1.79        | Powder        | Ba²⁺ doped   | 97%; 1 h Benzene removal under visible light, hydrothermally synthesised | [44]       |
| BiFeO₃-PbTiO₃             | 2.21        | Powder        | –            | \( k = 0.012 \text{ min}^{-1} \) Degradation of RhB under simulated solar light, | [97]       |
| BaTiO₃                    | 3.18 [26]   | Powder        | –            | \( k = 0.0036 \text{ min}^{-1} \) Degradation of RhB under AM 1.5 simulated solar light, Solid state synthesised powder | [14]       |
|                           | 3.14 [26]   | Powder        | Ag Co-catalyst| \( k = 0.087 \text{ min}^{-1} \) Degradation of RhB under AM 1.5 simulated solar light, Solid State synthesised powder | [14]       |
| BaTiO₃−α-Fe₂O₃            | 3.0 [72]    | Core-shell    | 0.01M of Fe(NO₃)₃·9H₂O | \( k = 0.0153 \text{ min}^{-1} \) Degradation of RhB under simulated solar light | [98]       |
| BaTiO₃−TiO₂               | 3.2         | Core-shell    | –            | \( \approx 80\%:2 \text{ h} \) RhB Degradation of RhB under UV light (280-400 nm) Hydrothermally synthesised | [99]       |
| PbTiO₃                    | 2.75        | Powder        | Pt Co-catalyst| 27.4 \( \mu \text{mol H}_2 \cdot (\text{g H})^{-1} \) Flux synthesised powder, hydrogen generation under 400W Xe lamp \( \lambda > 300 \text{nm} \) | [29]       |
| PbTiO₃−TiO₃               | 3.08        | Platelets     | Epitaxially grown TiO₂ | \( k = 0.053 \text{ min}^{-1} \) Degradation of MB under visible light (\( \gtrsim 420 \text{nm} \)). Hydrothermally synthesised | [95]       |
| KNbO₃                     | 3.27 [100]  | Pellet        | Pd-Ag coated | \( k = 0.317 \text{ min}^{-1} \) Degradation of RhB under UV light, solid state synthesised pellet | [101]      |
| LiNbO₃                    | 3.7         | Powder        | –            | 12%; 1h RhB Degradation of RhB under simulated solar light, | [102]      |
| KNN                       | 4.28 [103]  | Powder        | –            | 0.47 mmol g⁻¹h⁻¹ Solid state synthesised powder, H₂ evolution in aqueous methanol solution under UV light. | [40]       |
| BiVO₄−BiFeO₃−CuInS₂       | 2.69 - 2.42 - 1.48 Multi-layer film Deposited on FTO substrate | \( k = 1.19 \text{hr} \) Degradation of 4-nitrophenol under visible light, Xe lamp (\( \gtrsim 420 \text{nm} \)) | [79]       |
| rGO−BaTiO₃                | 2.4         | Nanosheet     | –            | \( k = 0.0556 \text{ min}^{-1} \) Degradation of MB under visible light (\( \gtrsim 400 \text{nm} \)) | [68]       |
| g-C₃N₄−BiFeO₃             | 2.7         | Powder        | –            | \( k = 0.0129 \text{ min}^{-1} \) Degradation of RhB under 300W Xe lamp (\( \gtrsim 400 \text{nm} \)), hydrothermal BiFeO₃ synthesis | [104]      |
| Commercially Available Photovoltaic Modules with alkaline electrolyser | 1.14        | Solar Cell module | 1.129 mmol H₂ h⁻¹ Maximum hydrogen production rate using six commercially available monocrystalline silicon photovoltaic modules (STP160S-24/AC) in conjunction with alkaline electrolyser under natural solar irradiation | [3]        |
systems with impressive performance. In addition to would allow to improve clarity and highlight sys-
tematically. The introduction of a standard testing method for difficult to draw a direct comparison between ing performance of photocatalytic systems. It is there-
fore significant to note that variation in the experimental parameters when report-
ing performance in heterogeneous systems. The ability to increase the degree of band bending could significantly reduce the rate of recombination of photogenerated charge carriers therefore providing an enhancement in conversion efficiency. Recent progress in the field has led to unprecedented chemical and nanostructure control to address inherent challenges in ferroelectric photocatalysts, e.g. slow charge carrier mobility, hence improving performance. Through doping, charge transport within ferroelectric materials can be greatly improved. Furthermore, improvements in nanostructural design offer new opportunities to explore the effects of ferroelectric polarisation in new architectures. Such prospects have the potential to mitigate the limitations of photocatalytic performance in ferroelectric oxides while retaining modulated interfacial band bending.

**Summary**

In this review, the current understanding of the inter-
play between ferroelectric polarisation and photocat-
alytic performance is presented and discussed. The interaction of ferroelectric polarisation with interfa-
cial space charge regions is highlighted as a key aspect of photocatalytic performance in heterostructures. The ability to increase the degree of band bending could significantly reduce the rate of recombination of photogenerated charge carriers therefore providing an enhancement in conversion efficiency. Recent progress in the field has led to unprecedented chemical and nanostructure control to address inherent challenges in ferroelectric photocatalysts, e.g. slow charge carrier mobility, hence improving performance. Through doping, charge transport within ferroelectric materials can be greatly improved. Furthermore, improvements in nanostructural design offer new opportunities to explore the effects of ferroelectric polarisation in new architectures. Such prospects have the potential to mitigate the limitations of photocatalytic performance in ferroelectric oxides while retaining modulated interfacial band bending.

**Outlook**

There are evidently numerous promising avenues to incorporating ferroelectric materials in photocatalytic systems. Non-more so than the core–shell systems. These have been shown to bolster charge separation within materials with superior optical properties. It is generally accepted that no single material satisfies all requirements for a commercial ferroelectric photocatalyst. Therefore, the core–shell structure apportions the material demands to either the core or shell. This in turn broadens the range of possible candidate materials. In order to provide commercially viable sys-
tems a deeper understanding of charge transfer at the core–shell interface is required. Furthermore, the effect of ferroelectric polarisation at the nanoscale requires elucidation ideally by in-situ observation of photocat-
alytic processes at domain surfaces.

As shown evident in Table 1, there is significant variation in the experimental parameters when reporting performance of photocatalytic systems. It is therefore difficult to draw a direct comparison between reports. The introduction of a standard testing method would allow to improve clarity and highlight systems with impressive performance. In addition to experimental methodology the use of the theoreti-
cal simulations offers potential for new photocatalysts. Through machine learning, the suitable ferroelectric materials may be highlighted reducing the amount of time-consuming experimental research required.

The field of photocatalysis is one with a core focus of sustainability both in terms of energy dependency and environmental impact. To this end, the removal toxic materials such as lead as well as dependence on rare earth metals will be a key consideration in future years. Earth-abundant alternatives such as r-GO show great promise but need significant development.

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**References**

[1] Fuel Cells and Hydrogen Joint Undertaking. Hydro-
gen roadmap Europe: a sustainable pathway for the European energy transition. Publications Office; 2019.

[2] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature. 1972;238:37–38.

[3] Kovač A, Marciauč D, Budin L. Solar hydrogen production via alkaline water electrolysis. Int J Hydrogen Energy. 2019;44(20):9841–9848.

[4] Bhandari R, Shah RR. Hydrogen as energy carrier: techno-economic assessment of decentralized hydrogen production in Germany. Renew Energy. 2021;177:915–931.

[5] Feng Y, Li H, Ling L, et al. Enhanced photocatalytic degradation performance by fluid-induced piezoelec-
tric field. Environ Sci Technol. 2018;52:7842–7848.

[6] Zhao Y, Huang X, Gao F, et al. Study on water split-
ting characteristics of CdS nanosheets driven by the coupling effect between photocatalysis and piezoelec-
tricity. Nanoscale. 2019;11:9085–9090.

[7] Yu D, Liu Z, Zhang J, et al. Enhanced catalytic perform-
ce by multi-field coupling in KNbO3 nanostruk-
tures: piezo-photocatalytic and ferro-photoelectrochemi-
ic effects. Nano Energy. 2019;58:695–705.

[8] Chao C, Zhou Y, Han T, et al. Ferroelectric polariza-
tion-enhanced photocatalytic properties and photo-induced charge carrier behavior of Au/BaTiO3. J Alloys Compd. 2020;825:154060.

[9] Chen F, Huang H, Guo L, et al. The role of polar-
ization in photocatalysis. Angew Chemie Int Ed. 2019;58:2–15.

[10] Huang H, Tu S, Du X, et al. Ferroelectric sponta-
neous polarization steering charge carriers migration...
for promoting photocatalysis and molecular oxygen activation. J Colloid Interface Sci. 2018;509:113–122.

[11] Li L, Yang L, Xiong Y, et al. Impact of ferroelectric polarization on different semiconductors for photo-electrochemical application. ACS Sustain Chem Eng. 2019;7:19640–19648.

[12] Fang L, You L, Liu J-M. Ferroelectric materials for energy applications. 1st ed. Weinheim: Wiley-VCH; 2018.

[13] Huang G, Zhang G, Gao Z, et al. Enhanced visible-light-driven photocatalytic activity of BiFeO3 via electric-field control of spontaneous polarization. J Alloys Compd. 2019;783:943–951.

[14] Cui Y, Briscoe J, Dunn S. Effect of ferroelectricity on solar-light-driven photocatalytic activity of BaTiO3 - Influence on the carrier separation and stern layer formation. Chem Mater. 2013;25(21):4215–4223.

[15] Li L, Salvador PA, Rohrer GS. Photocatalysts with internal electric fields. Nanoscale. 2014;6:42–42.

[16] Pan L, Liu X, Sun Z, et al. Nanophotocatalysts via microwave-assisted solution-phase synthesis for efficient photocatalysis. J Mater Chem A. 2013;1(29):8299–8326.

[17] Guo L, Yang Z, Marcus K, et al. Mos 2/TiO2 heterostructures as nonmetal plasmonic photocatalysts for highly efficient hydrogen evolution. Energy Environ Sci. 2018;11:106.

[18] Xie S, Zhang Q, Liu G, et al. Photocatalytic and photoelectrocatalytic reduction of CO2 using heterogeneous catalysts with controlled nanostructures. Chem Commun. 2016;52:35.

[19] Damjanovic D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. Reports Prog Phys. 1998;61(9):1267–1324.

[20] Isohama Y, Nakajima N, Maruyama H, et al. Tetragonal-cubic phase transition in BaTiO3 probed by resonant X-ray emission spectroscopy. J Electron Spectros Relat Phenomena. 2011;184(3–6):207–209.

[21] Yang WC, Rodriguez BJ, Gruverman A, et al. Photo electron emission microscopy of polarity-patterned materials. J Phys Condens Matter. 2005;17(16):1415–1426.

[22] Li Y, Li J, Yang W, et al. Implementation of ferroelectric materials in photocatalytic and photo-electrochemical water splitting. Nanoscale Horiz. 2020;5(8):1174–1187.

[23] Jones PM, Dunn S. Interaction of Stern layer and domain structure on photochemistry of lead-zirconate-titanate. J Phys D Appl Phys. 2009;42(6):065408.

[24] Stock M, Dunn S. LiNbO3 - a new material for artificial photosynthesis. IEEE Trans Ultrason Ferroelectr Freq Control. 2011;58(9):1988–1993.

[25] Li D, Zhao MH, Garra J, et al. Direct in situ determination of the polarization dependence of physisorption on ferroelectric surfaces. Nat Mater. 2008;7(6):473–477.

[26] Cui Y, Goldup SM, Dunn S. Photodegradation of rhodamine B over Ag modified ferroelectric BaTiO3 under simulated solar light: pathways and mechanism. RSC Adv. 2015;5(58):30372–30379.

[27] Morris MR, Pendlebury SR, Hong J, et al. Effect of internal electric fields on charge carrier dynamics in a ferroelectric material for solar energy conversion. Adv Mater. 2016;28(33):7123–7128.

[28] GiocandJI, RohrerGS. Spatial separation of photochemical oxidation and reduction reactions on the surface of ferroelectric BaTiO3 3. J Phys Chem B. 2001;105(35):8275–8277.

[29] Arney D, Watkins T, Maggard PA. Effects of particle surface areas and microstructures on photocatalytic H2 and O2 production over PbTiO3. J Am Ceram Soc. 2011;94(5):1483–1489.

[30] ShabanaiZadeh S, Abedini A, Alborzi A, et al. Green synthesis and characterization of lead titanate nanoparticles and its photocatalyst application. J Mater. Sci. Mater. Electron. 2015;27(3):2589–2593.

[31] Inoue Y, Sato K, Sato K, et al. Photoassisted water decomposition by ferroelectric lead zirconate titanate ceramics with anomalous photovoltaic effects. J Phys Chem. 1986;90(13):2809–2810.

[32] Fridkin VM, Popov BN. Anomalous photovoltaic effect in ferroelectrics. Sov Phys Usp. 1978;21(981):657–671.

[33] Chen T, Meng J, Wu S, et al. Room temperature synthesized BaTiO3 for photocatalytic hydrogen evolution. J Alloys Compd. 2018;754:184–189.

[34] Su R, Shen Y, Li L, et al. Silver-modified nanosized ferroelectrics as a novel photocatalyst. Small. 2015;11(2):202–207.

[35] Zhou JP, Zhang L-Z, Luo S-L, et al. Preparation and photocatalytic activities of two new Zn-doped SrTiO3 and BaTiO3 photocatalysts for hydrogen production from water without cocatalysts loading. Int J Hydrogen Energy. 2012;37(22):17068–17077.

[36] Huang HC, Yang CL, Wang MS, et al. Chalcogens doped BaTiO3 for visible light photocatalytic hydrogen production from water splitting. Spectrochim Acta Part A Mol Biomol Spectros. 2019;208:65–72.

[37] Maeda K. Rhodium-doped barium titanate perovskite as a stable p-type semiconductor photocatalyst for hydrogen evolution under visible light. ACS Appl Mater Interfaces. 2014;6:2167–2173.

[38] Yu J, Chen Z, Zeng L, et al. Synthesis of carbon-doped KNbO3 photocatalyst with excellent performance for photocatalytic hydrogen production. Sol Energy Mater Sol Cells. 2018;179:45–56.

[39] Van Beveren W. Lead-free piezoceramics. Nature. 2004;432:84–87.

[40] Park S, Lee CW, Kang M-G, et al. A ferroelectric photocatalyst for enhancing hydrogen evolution: polarized particulate suspension. Phys Chem Chem Phys. 2014;16:10408–10413.

[41] Lebeugle D, Colson D, Forget A, et al. Very large spontaneous polarization in BaTiO3 single crystals at room temperature and its evolution under cycling fields. Appl Phys Lett. 2007;91(2):2004–2007.

[42] Sando D, Carréréro C, Grisolia MN, et al. Revisiting the optical band gap in epitaxial BiFeO3 thin films. Adv Opt Mater. 2018;6(2):1–13.

[43] Meng W, Hu R, Yang J, et al. Influence of lanthanum-doping on photocatalytic properties of BiFeO3 for phenol degradation. Cuihua Xuebao/Chinese J Catal. 2016;37(9):1283–1292.

[44] Soltani T, Lee BK. Novel and facile synthesis of Ba-doped BiFeO3 nanoparticles and enhancement of their magnetic and photocatalytic activities for complete degradation of benzene in aqueous solution. J Hazard Mater. 2016;316:122–133.

[45] Rojac T, Bencan A, Malic B, et al. BiFeO3 ceramics: processing, electrical, and electromechanical properties. J Am Ceram Soc. 2014;97(7):1993–2011.

[46] Arora M, Sati PC, Chauhan S, et al. Structural, optical and multiferroic properties of BiFeO3 nanoparticles.
synthesized by soft chemical route. J Supercond Nov Magn. 2013;26(2):443–448.

[47] Han H, Lee JH, Jang HM. Low-temperature solid-state synthesis of high-purity BiFeO3 ceramic for ferroic thin-film deposition. Inorg Chem. 2017;56(19): 11911–11916.

[48] Liu T, Xu Y, Feng S, et al. A facile route to the synthesis of BiFeO3 at low temperature. J Am Ceram Soc. 2011;94(9):3060–3063.

[49] Srivastav SK, Gajbhiye NS. Low temperature synthesis, structural, optical and magnetic properties of bismuth ferrite nanoparticles. J Am Ceram Soc. 2012;95(11):3678–3682.

[50] Deng J, Banerjee S, Mohapatra SK, et al. Bismuth iron oxide nanoparticles as photocatalyst for solar hydrogen generation from water. J Funam Renew Energy Appl. 2011;1:1–10.

[51] Basith MA, Yesmin N, Hossain R. Low temperature synthesis of BiFeO3 nanoparticles with enhanced magnetization and promising photocatalytic performance in dye degradation and hydrogen evolution. RSC Adv. 2018;8(52):29613–29627.

[52] Gao F, Yuan Y, Wang KF, et al. Preparation and photoabsorption characterization of BiFeO3 nanowires. Appl Phys Lett. 2006;89:102506.

[53] Li S, Zhang J, Kibria MG, et al. Remarkably enhanced photocatalytic activity of Gd-doped BiFeO3 nanowires under visible-light. Chem Commun. 2013;49(52):5856–5858.

[54] Zhang N, Chen D, Niu F, et al. Enhanced visible light photocatalytic activity of Gd-doped BiFeO3 nanoparticles and mechanism insight. Sci Rep. 2016;6:1–11.

[55] Yang Y, Kang L, Li H. Enhancement of photocatalytic hydrogen production of BiFeO3 by Gd 3+ doping. Ceram Int. 2019;45(6):8017–8022.

[56] Tan H, Zhao Z, Zhu W-b, et al. Oxygen vacancy enhanced photocatalytic activity of pervoskite SrTiO3. ACS Appl Mater Interfaces. 2014;6(21):19184–19190.

[57] Haruna A, Abdulkadir I, Idris SO. Photocatalytic activity and doping effects of BiFeO3 nanoparticles in model organic dyes. Heliyon. 2020;6(1):e03237.

[58] Ponraj C, Vinitha G, Daniel J. A review on the visible light active BiFeO3 nanostructures as suitable photocatalyst in the degradation of different textile dyes. Environ Nanotechnol Monit Manag. 2017;110–120.

[59] Gao F, Chen X Y, Yin K B, et al. Visible-light photocatalytic properties of weak magnetic BiFeO3 nanoparticles. Adv Mater. 2007;19(19):2889–2892.

[60] Chen D, Niu F, Qin L, et al. Defective BiFeO3 with surface oxygen vacancies: facile synthesis and mechanism insight into photocatalytic performance. Sol Energy Mater Sol Cells. 2017;171:24–32.

[61] Hengky C, Moya X, Mathur ND, et al. Evidence of high rate visible light photochemical decolourisation of Rhodamine B with BiFeO3 3 nanoparticles associated with BiFeO3 photocorrosion. RSC Adv. 2012;2(31):11843–11849.

[62] Huo Y, Jin Y, Zhang Y. Citric acid assisted solvothermal synthesis of BiFeO3 microspheres with high visible-light photocatalytic activity. J Mol Catal A Chem. 2010;331(1–2):15–20.

[63] Wang H, Zhang L, Chen Z, et al. Semiconductor heterojunction photocatalysts: design, construction, and photocatalytic performances. Chem Soc Rev. 2014;43(15):5234–5244.

[64] Jiang C, Moniz SIA, Wang A, et al. Photoelectrochemical devices for solar water splitting—materials and challenges. Chem Soc Rev. 2017;46:4645.

[65] Huang BC, Chen YT, Chiu YP, et al. Direct observation of ferroelectric polarization-modulated band bending at oxide interfaces. Appl Phys Lett. 2012;100(122903):1–4.

[66] Ran J, Zhang Y, Yu J, et al. Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. Chem Soc Rev. 2014;43(22):7787–7812.

[67] Guo Y, Zhou S, Sun X, et al. Synthesis and photocatalytic activity of BiFeO3 and Bi/BiFeO3 cubic microcrystals. J Am Ceram Soc. 2020;103(8):4122–4128.

[68] Jiang S, Zhao R, Ren Z, et al. A reduced graphene oxide (rGO)-ferroelectrics hybrid nanocomposite as high efficient visible-light-driven photocatalyst. Chemistry-Select. 2016;1(18):6020–6025.

[69] Di Valentin C, Pacchioni G. Trends in non-metal doping of anatase TiO2: B, C, N and F. Catal Today. 2013;206:12–18.

[70] Shi J, Zhao P, Wang X. Piezoelectric-polarization-enhanced photovoltaic performance in depleted-heterojunction quantum-dot solar cells. Adv Mater. 2013;25(6):916–921.

[71] Samran B, Lunput S, Tonnonchiang S, et al. BiFeO3 /BiVO4 nanocomposite photocatalysts with highly enhanced photocatalytic activity for rhodamine B degradation under visible light irradiation. Phys B Condens Matter. 2019;561:23–28.

[72] Cui Y, Briscoe J, Wang Y, et al. Enhanced photocatalytic activity of heterostructured ferroelectric Bi4Ti3O12–FePO3 and the significance of interface morphology control. ACS Appl Mater Interfaces. 2017;9(29):24518–24526.

[73] Huang H, Li D, Lin Q, et al. Efficient photocatalytic activity of PZT/TiO2 heterojunction under visible light irradiation. J Phys Chem C. 2009;113(32):14264–14269.

[74] Niu F, Chen D, Qin L, et al. Facile synthesis of highly efficient p-n heterojunction CuO/BiFeO3 composite photocatalysts with enhanced visible-light photocatalytic activity. ChemCatChem. 2015;7(20):3279–3289.

[75] Osterloh FE. Inorganic nanostructures for photoelectronic devices for solar watersplitting—materials and challenges. ChemSocRev. 2014;43(22):7787–7812.

[76] Afroz K, Moniruddin M, Bakranov N, et al. A hetero-junction strategy to improve the visible light sensitive water splitting performance of photocatalytic materials. J Mater Chem A. 2018;6(44):21696–21718.

[77] Stolarczyk JK, Bhattacharyya S, Polavarapu L, et al. Challenges and prospects in solar water splitting and CO2 reduction with inorganic and hybrid nanostructures. ACS Catal. 2018;8(4):3602–3635.

[78] Li H, Quan X, Chen S, et al. Ferroelectric-enhanced Z-schematic electron transfer in BiVO4·BiFeO3–CuInS2 for efficient photocatalytic pollutant degradation. Appl Catal B Environ. 2017;209:591–599.

[79] Di L, Yang H, Xian T, et al. Photocatalytic and photo-fenton catalytic degradation activities of Z-scheme Ag 2 S/BiFeO3 3 heterojunction composites under visible-light irradiation. Nanomaterials. 2019;9(3):399.

[80] Wu M, Ding T, Wang Y, et al. Rational construction of plasmon Au assisted ferroelectric-BaTiO3 /Au/g-C 3 N 4 Z-scheme system for efficient photocatalysis. Catal Today. 2019;355:311–318.
[82] Ong WJ, Tan LL, Ng YH, et al. Graphitic carbon nitride (g-C3N4)-based photocatalysts for artificial photosynthesis and environmental remediation: are we a step closer to achieving sustainability? Chem Rev. 2016;116(12):7159–7329.

[83] Sepahvand H, Sharifinia S. Photocatalytic overall water splitting by Z-scheme g-C3N4/BiFeO3 heterojunction. Int J Hydrogen Energy. 2019;44(42):23658–23668.

[84] Li L, Rohrer GS, Salvador PA. Heterostructured ceramic powders for photocatalytic hydrogen production: Nanostructured TiO2 shells surrounding microcrystalline (Ba, Sr) TiO3 cores. J Am Ceram Soc. 2012;95(4):1414–1420.

[85] Li L, Zhang Y, Schultz AM, et al. Visible light photochemical activity of heterostructured PbTiO3-3-TiO2 2 core-shell particles. Catal Sci Technol. 2012;2(9):1945–1952.

[86] Li L, Liu X, Zhang Y, et al. Visible-light photochemical activity of heterostructured core−shell materials composed of selected ternary titanates and ferrites coated by TiO2. ACS Appl Mater Interfaces. 2013;5(11):5064–5071.

[87] Luttrell T, Halpegamage S, Tao J, et al. Why is anatase a better photocatalyst than rutile? - Model studies on epitaxial TiO2 films. Sci Rep. 2015;4(1):1–8.

[88] Liu H, Zhang Y, Zhang X, et al. Tuning the structural distortion and visible-light-driven photocatalytic properties of LaCoO3 thin films by epitaxial strain. J Alloys Compd. 2019;777:679–687.

[89] Yang M-M, Luo Z-D, Kim DJ, et al. Bulk photovoltaic effect in monodomain BiFeO3 thin films. Appl Phys Lett. 2017;110:183902.

[90] Magnan H, Deleuze PM, Brehin J, et al. Tuning the charge carriers migration in epitaxial BaTiO3 thin-film photoanodes. J Phys Chem C. 2020;124(19):10315–10323.

[91] Ji W, Yao K, Lim YF, et al. Epitaxial ferroelectric BiFeO3 thin films for unassisted photocatalytic water splitting. Appl Phys Lett. 2013;103(6):1–5.

[92] Chen XY, Yu T, Gao F, et al. Application of weak ferromagnetic BiFeO3 films as the photoelectrode material under visible-light irradiation. Appl Phys Lett. 2007;91(2):10–13.

[93] Xu HM, Wang HC, Shen Y, et al. Photocatalytic and magnetic behaviors of BiFeO3 thin films deposited on different substrates. J Appl Phys. 2014;116(17):1–6.

[94] Li D, Song H, Meng X, et al. Effects of particle size on the structure and photocatalytic performance by alkali-treated TiO2. Nanomaterials. 2020;10(3):1–14.

[95] Li W, Wang F, Li M, et al. Polarization-dependent epitaxial growth and photocatalytic performance of ferroelectric oxide heterostructures. Nano Energy. 2018;45:304–310.

[96] Yang W, Yu Y, Starr MB, et al. Ferroelectric polarization-enhanced photoelectrochemical water splitting in TiO2-BaTiO3 core-shell nanowire photoanodes. Nano Lett. 2015;15(11):7574–7580.

[97] Narayan B, Adhikari S, Madras G, et al. Trapping a metastable ferroelectric phase by size reduction in semiconducting ferroelectric BiFeO3 3-PbTiO3 3 and its implications for photocatalytic response. Phys Rev Appl. 2017;7(2):024018.

[98] Cui Y, Sun H, Briscoe J, et al. Influence of ferroelectric dipole on the photocatalytic activity of heterostructured BaTiO3-a-Fe2O3. Nanotechnology. 2019;30:255702.

[99] Liu X, Lv S, Fan B, et al. Ferroelectric Polarization-Enhanced photocatalysis in BaTiO3-TiO2 core-shell heterostructures. Nanomaterials. 2019;9(8):1116.

[100] Zlotnik S, Tobaldi DM, Seabra P, et al. Alkali niobate and tantalate perovskites as alternative photocatalysts. ChemPhysChem. 2016;17(21):3570–3575.

[101] Fu Q, Wang X, Li C, et al. Enhanced photocatalytic activity on polarized ferroelectric KNbO3. RSC Adv. 2016;6:108883–108887.

[102] Stock M, Dunn S. Influence of the ferroelectric nature of lithium niobate to drive photocatalytic dye decolorization under artificial solar light. J Phys Chem C. 2012;116:20854–20859.

[103] Rani J, Patel PK, Adhlakha N, et al. Mo6+ modified (K0.5Na0.5)NbO3 lead free ceramics: structural, electrical and optical properties. J Mater Sci Technol. 2014;30(5):459–465.

[104] Fan T, Chen C, Tang Z, et al. Synthesis and characterization of g-C3N4/BiFeO3 composites with an enhanced visible light photocatalytic activity. Mater Sci Semicond Process. 2015;40:439–445.