



Routes to energy conversion with functional oxide films and nanostructures, a short review



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ABSTRACT

In the last 10 years there has been growing interest to investigate the impact of non-centrosymmetry of piezo or ferroelectric materials for energy harvesting devices and systems. There are a large range of devices being investigated including those that convert kinetic energy into electrical energy or convert sunlight into fuels, known as solar fuels, or produce electrical energy such as in a photovoltaic device. The fundamental principle and area of interest in these materials are related to the breaking of crystal symmetry found in a piezo or ferroelectric material. This breaking of crystal symmetry intimately influences the physical properties within the material and leads to some specific behaviour. We know that the domain structure of a ferroelectric material separates photoinduced carriers that lead to regio-specific photochemistry.

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Oxidation and reduction can occur on predefined areas of the photocatalyst surface, separated by tens to hundreds of nanometres, when it is ferroelectric. This result might at first sight seem quite surprising given the low mobility of carriers and shallow penetration of light into a ferroelectric material [1]. However, when considered in the context of a photoelectrochemical cell where ionic species are charge carriers there are remarkable similarities. The band bending induced when a non-polar semi-conductor contacts an electrolyte of differing redox potential to the Fermi level of the semiconductor induces a similar movement of carriers to that found in a ferroelectric material. In the ferroelectric the movement of carriers is due to dipole found in the crystal lattice. By focusing on the process of the polar interaction of a ferroelectric lattice and the means by which it can enhance photocatalytic efficiency we can extend the analogy still further. The phenomena responsible for the increase in power conversion efficiency in a ZnO based photovoltaic device [2] when acoustically stimulated convert vibration, or kinetic energy, into an electrical output. In the case of ZnO the kinetic energy generates an oscillating electric field which increases performance due to improved carrier separation.

Since the mid-20th century there has been interest in using ferro/piezoelectric materials for devices. There are some extremely common applications of ferroelectric $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) and BaTiO_3 surrounding us in every day usage. For example, 3D ultrasound systems rely on ferroelectric materials for both actuation and sensing and the high performance of modern diesel engines and inkjet printer heads benefit from the direct piezoelectric. Around 2000 there were efforts to use the

depolarisation field of a ferroelectric to control liquid crystal displays [3] as at that time it was shown that virus particles could be directed to physisorb at a pre-determined location on the surface of a ferroelectric material [4]. There was ongoing work that showed that the influence of the ferroelectric dipole could drive photoexcited carriers in a ferroelectric and showed spatially selective photochemistry. Inoue et al. reported that different ferroelectric domains could drive photochemistry over a film of titania on the surface of a ferroelectric material [5] for photoassisted water splitting. This was then followed by the work of Giocondi and Rohrer [6,7] showing that the photochemistry on bulk ferroelectric materials was domain specific, as shown in Fig. 1. This work was soon followed by that of Kalinin et al. [8] who used a sample of PZT patterned with an atomic force microscope to show that there was a level of control over the redox chemistry for a ferroelectric system. An example of the fidelity of the redox processes can be seen in Fig. 2.

The fundamental physics behind carrier separation in the ferroelectric material occurs due to the development of a space charge layer resulting from the movement of mobile carriers screening remnant polarisation (P_r) [9]. A description of the influence of depolarisation field on development of a space charge layer is given in Fig. 3. Additionally, there is a strong interaction with the surface of the ferroelectric and any species that are in contact with the surface [10]. The extent of this interaction has been demonstrated with Langmuir desorption [11,12] isotherms showing an intimate relationship between the surface charge and gaseous species at the surface. It is this surface interaction and spatially selective redox chemistry that make ferroelectric materials an interesting class of materials for used photocatalysts or incorporated into a photovoltaic device.

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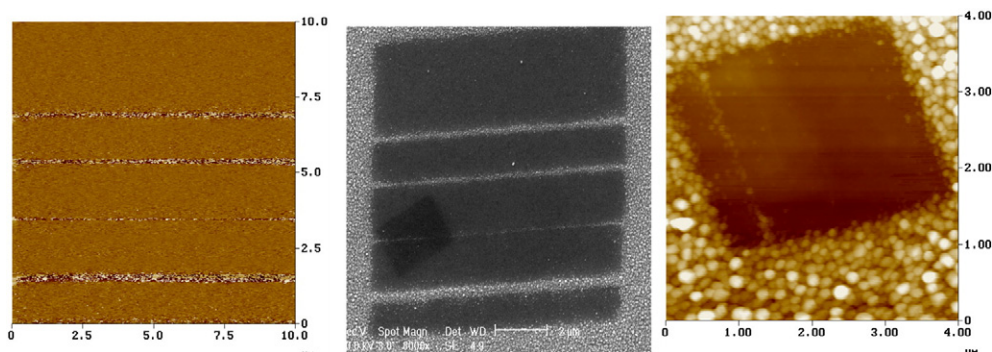


Fig. 1. AFM images (piezo force microscopy set left and topography set right) showing the surface of $\text{Pb Zr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ before (left) and after decoration (middle and right) with Ag^0 through photochemical reaction. The Ag^0 has deposited on the domains of $\text{Pb Zr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ where electrons are driven to the surface due to the dipole in the crystal lattice.

For example LiNbO_3 is strongly ferroelectric [13] possessing a surface charge of tens of $\mu\text{C}/\text{cm}^2$ with a highly reducing conduction band that has been shown to reduce Al^{3+} to Al^0 under visible light illumination [14]. This is a somewhat surprising result as although there was little super bandgap light in the solar spectrum there was still a significant rate of deposition of Al^0 on the ferroelectric substrate. The exact reasons for this were postulated to be due to the effective separation of carriers resulting in disparate redox reaction centres. The interest in LiNbO_3 does not end with investigating the photochemical interactions of ionic species on LiNbO_3 . There have been detailed studies that show an interaction between the dipole of LiNbO_3 and the electron affinity found in the material [15,16] [12] as well investigations using LiNbO_3 as a solar fuel catalyst [17,18,19]. In cases where LiNbO_3 has been used as a visible light photocatalyst the explanation for the activity has been associated with enhanced carrier separation and surface interactions [20] and recently pyroelectric interactions [21].

Ferroelectric materials with band gaps approaching 3 eV are of greater interest for use as a visible light photocatalyst. While photons exceeding 3 eV contribute only 4–5% of the terrestrial solar spectrum improving the quantum efficiency (external quantum efficiency – EQE) of a system by driving the reaction equilibrium towards products by removing back reactions or increasing the effective light harvesting ability of the catalyst is highly advantageous. The key material of interest to date has been BaTiO_3 (BTO) [22–24] which is a prototypical ferroelectric system. There are advantages to using BTO as it is very well characterised and readily available from commercial suppliers. A further advantage of BTO is the ability to control the ferroelectric nature of the material through size [25,26] and a Curie temperature that is readily accessible at around 130 °C. It has been recently demonstrated that the

ferroelectric nature of BTO can significantly enhance the photochemical activity of an otherwise reasonably inert material, and that the photochemical performance of BTO is further enhanced with the addition of a nanostructured metal [27], Fig. 4.

In addition to BTO, BiFeO_3 (BFO) has been studied as a photocatalyst or incorporated into a photovoltaic device [28–31]. BFO is an interesting, or frustrating material depending on your end application, that has been variously described in the literature as having a direct, indirect band gap with a band gap reported from 2 to 3 eV or as a p or indeed n-type [32] material. There remain a number of key unanswered questions regarding BFO and many of these have been difficult to answer as until very recently there have been no reliable methods for synthesising nanostructured thin films. However, recent work from UNSW show that it is possible to make high quality BFO thin films [33], which now opens a pathway to a series of more in depth studies.

An interesting study by Barbure et al. has shown [22] that the dipole of a ferroelectric material can penetrate a non-polar semiconductor and influence the photochemistry at the interface. BaTiO_3 was coated with

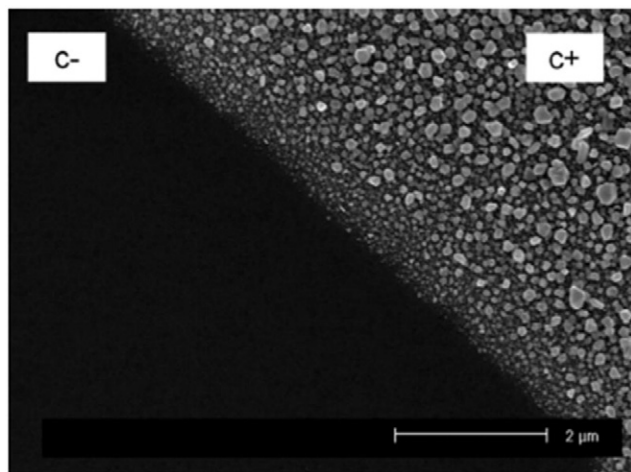


Fig. 2. A clear association between the patterned PZT and deposition of Ag^0 after reduction of Ag^+ with a photoexcited electron in the PZT conduction band.

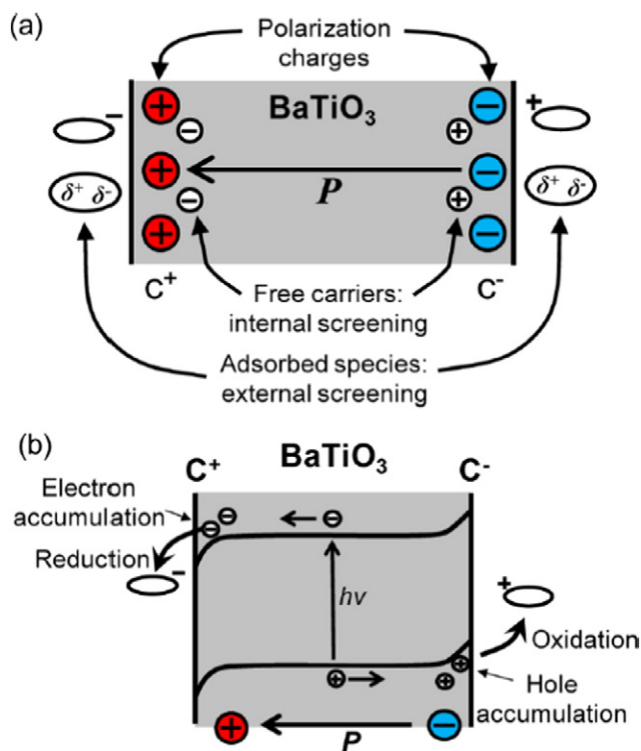


Fig. 3. Indicating the screening mechanisms and associated motion of mobile carriers (a) that results in the development of a space charge layer and resultant selective photochemistry (b).

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