

Chapter 2

Literature Review

This chapter discusses the use of titanium dioxide as the active material in photo-electrochemical cells for the electrolysis of water, with the aim of producing a source of renewable hydrogen. Recent reports of sensitizing TiO_2 to visible light using localized surface plasmon resonance (LSPR) on metal nanoparticles are discussed.

The choice of titanium dioxide as a material for water splitting was due to its stability as an n-type semiconductor, the extensive literature on its photo-electrochemical behaviour and, in the wider project at Imperial College London, the development of a parallel stream of computational descriptions of the surfaces of rutile and anatase (EPSRC Programme Grant on Nanostructured Functional Materials for Energy Efficient Refrigeration, Energy Harvesting and Production of Hydrogen from Water).

The global context driving interest in photo-electrochemical hydrogen production by water splitting is introduced in Sect. 2.1, followed by a basic overview of photo-electrochemical cells (PECs), with a more detailed treatment in the following chapter Principles of Photo-Electrochemical Cells. The main requirements for a water splitting material are introduced in Sect. 2.3, and the use of metal oxides is introduced in Sect. 2.4.

In Sect. 2.5, the concept of ‘plasmonic water splitting’ is introduced, followed by a brief outline of plasmonic resonance on metal nanoparticles in Sect. 2.6. Fabrication methods for metal nanoparticles are discussed in Chap. 4, Experimental Methods. The bulk of the literature review covers the use of gold nanoparticles (AuNPs) to “enhance” the performance of TiO_2 (both rutile and anatase). Various experimental reports are discussed in Sect. 2.7 followed by a critical discussion of the proposed mechanisms of “plasmonic enhancement” in Sects. 2.8–2.10. The published data reviewed and discussed in this chapter led to the experimental work reported in Chaps. 5 and 6 of this thesis. The purpose of this work was to detect the reported effect, and to try to determine and understand the mechanisms involved.

In Sect. 2.11, the literature review also includes a brief summary of reports on the growth of oriented and epitaxial thin films of anatase and rutile for a range of

purposes. These were used as a starting point for determining the growth conditions for rutile and anatase thin films, as reported in Chaps. 7 and 8 of this thesis, aiming to provide high quality surfaces to support theoretical models based on hybrid density functional theory (h-DFT), undertaken in the same Programme Grant.

Finally, Sect. 2.12 presents a review of the theoretical defect chemistry of TiO_2 , aiming to understand why heavily doped anatase and rutile films grown during this project did not show the levels of conductivity reported by other authors. The interpretation of this theory in the context of the doped films is reported in Chap. 7, TiO_2 films on fused silica.

In Chap. 4, Experimental Methods, a range of experiments are outlined in response to this review of the literature.

2.1 Global Energy Drivers for Solar Water Splitting

During the 21st Century, the world population is expected to increase to a peak of 9 billion, while demand for energy will also increase as people aspire to a Western standard of living [1, 2]. Against a background of increased energy demand, reducing carbon dioxide emissions to prevent climate change is a significant global challenge [3]. For example, the UK has committed to 80 % reduction compared with 1990 levels by 2050 [4]. Low-carbon and renewable energy sources, such as wind and solar power, will be crucial in meeting this target. One of the major drawbacks of renewable energy sources is intermittency: solar technologies such as photovoltaic (PV) cells are affected by weather and the fact that the sun only shines on half of the surface of the Earth at any one time. As such, without energy storage technology, power output is unlikely to match demand [5, 6].

Conversion of electrical energy into a ‘solar fuel’ is one possible approach to using energy storage to mitigate this intermittency. One of the main candidates for a solar fuel is hydrogen (H_2), which can be produced by the electrolysis of water. Hydrogen is a versatile fuel—it can be used in both fuel cells and combustion engines—with the only combustion products being water vapour and heat [7]. As such, it also presents an alternative to hydrocarbons for transport, provided hydrogen storage can be made more efficient and economic. The wide-scale adoption of H_2 as a fuel for transport and energy storage is known as the Hydrogen Economy [8]. Currently, most H_2 is produced by steam reforming of natural gas, which produces CO_2 and largely negates the benefits on offer. Renewable and carbon-free H_2 production is possible by using PV generated electricity to power a separate electrolyser (alkaline or PEM).

An alternative approach is to simultaneously harvest sunlight and produce hydrogen in a photo-electrochemical cell (PEC) employing materials such as TiO_2 and Fe_2O_3 as photo-anodes. The potential benefit is decreased material and equipment cost, as the area of solar collector also acts as the electrode (although this has yet to be demonstrated in practice). As H_2 would compete with battery technology for electricity storage, another potential market for H_2 is as a chemical

feedstock for ammonia production and/or to help reduce CO_2 to a fuel in an Artificial Leaf.¹

At present, there are no commercialized PEC systems for photo-electrolysis of water (water-splitting), although devices with up to 16 % solar-to-hydrogen (STH) efficiency have been produced by employing a $\text{GaInP}_2/\text{GaAs}$ multi-junction cell [9]. However, devices using these rare III–V semiconducting materials are prohibitively expensive and unstable in aqueous environments, so are unsuitable for large-scale commercialization. Although Si is also unstable in oxidizing environments, even in water, a promising Si-based device has been reported [10] with efficient Co catalysts, forming a stable photo-anode for water splitting. The fundamental advantage of Si is that, with a band gap of ca. 1.1 eV, it is a good absorber of sunlight, in principle enabling high efficiencies. The challenges are in catalysing the reactions, and material stability.

However, devices employing cheap, earth-abundant materials that are stable in water, such as metal oxides, suffer from low efficiencies, due to large band gaps, conduction band edge energies that will not reduce H^+ to H_2 , and poor electron-hole (e^-h^+) lifetimes [11]. The focus of the work reported in this thesis was to investigate routes to improving the understanding and performance of metal oxides, especially titanium dioxide, for water splitting applications. In the following discussion, brief reference will also be made to hematite (Fe_2O_3), which was also studied during the research period.

2.2 Photo-Electrochemical Cells (PECs)

The basic principles of PECs are discussed, followed by consideration of the materials TiO_2 and Fe_2O_3 for successful water splitting. The explanations that follow are based on photo-anodes, at which the oxidation of water occurs by the oxygen evolution reaction (OER). A photo-anode is formed by an n-type semiconductor, such as TiO_2 or Fe_2O_3 in contact with a redox couple in electrolyte. Further detail on the structure of the semiconductor-liquid interface and the terminology used may be found in the Chap. 3 of this thesis, Principles of Photo-electrochemical Cells.

2.2.1 Overview

The components of a basic n-type photo-electrochemical cell (PEC) are illustrated in Fig. 2.1. A PEC for water splitting consists of a semiconductor photo-anode, an aqueous electrolyte, a counter electrode, and an ohmic contact that transports

¹See <http://www3.imperial.ac.uk/energyfutureslab/research/grandchallenges/artificialleaf>.

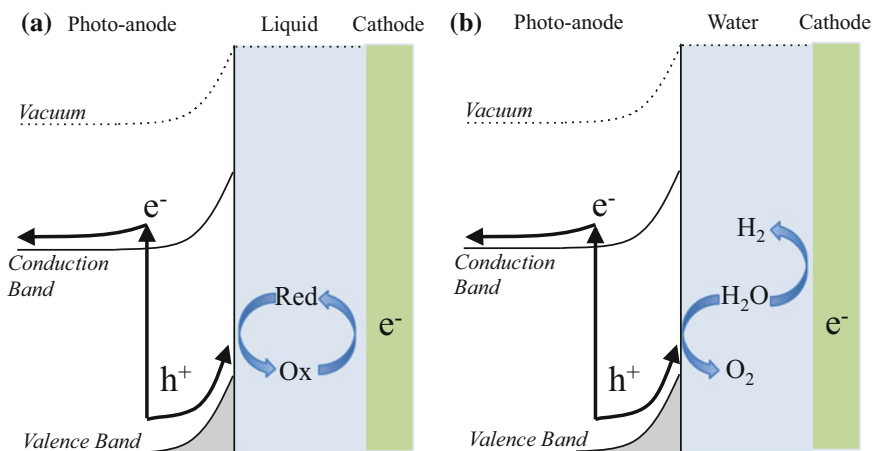


Fig. 2.1 Basic schematic diagram of (a) a regenerative PEC and (b) a hydrogen producing PEC. Image based on publication [12]

electrons from the semiconductor to the counter electrode (or cathode), where they reduce protons/water to hydrogen. In the case of a photo-anode, the electron and hole are generated by the absorption of a photon. In Fig. 2.1a, a reductant (Red) is oxidized at the photoanode of a regenerative PEC by a hole (h^+) and becomes an oxidant. The oxidant (Ox) diffuses to the counter electrode (cathode or photo-cathode) and is reduced by an electron (e^-) to its original state i.e. the process is regenerative. In the case of a water splitting cell (Fig. 2.1b), the oxidation of water/ OH^- results in the generation of oxygen, which leaves the PEC. Likewise, the reduction of water/ H^+ results in the generation of hydrogen, which leaves the PEC. The reaction is not regenerative; water is consumed in the production of hydrogen.

Practically, the O_2 and H_2 must be generated and separated in the cell to avoid the spontaneous reverse reaction. In a PEC with a photoactive anode (as in the case of TiO_2 and Fe_2O_3), the H^+ ions (protons) produced by OER reaction must be transported away from the photo-anode by a conductive electrolyte to the cathode for reduction. A typical means of ensuring separation is the use of a proton exchange membrane (PEM) which allows protons to pass, but prevents electrons and OH^- ions doing so. Alternatively, if the photocathode was the driving force, then the OH^- ions must be transported to an anode for oxidation [13, 14]. In some water splitting ‘Z-schemes’, both a photo-anode and a photo-cathode are employed together to boost the fraction of light absorbed [13, 15] and to provide sufficient electrical potential to drive water splitting.

Materials produced and investigated in this project were for use as photo-anodes in a PEC. This means that the practicalities of PEC operation need to be borne in mind when proposing new material systems. These considerations include: efficiency targets for a real-world technology; possible efficiency limits in proposed

systems; and electron and hole potentials relative to the potentials of redox couples. Other issues such as charge separation, lifetime and mobility also need to be considered.

2.3 Requirements for Economical PEC Water Splitting

To assess the suitability of materials and systems for economically feasible water splitting, it is necessary to be efficient, cheap and robust, which may be summarised in scientific terms as: generate sufficient photo-potential to split water; generate sufficient photocurrent to efficiently produce hydrogen; be stable, i.e. not be decomposed by electrons, holes, hydroxide ions or protons; and do so cheaply [15]. The first two requirements are discussed below in more detail in relation to TiO_2 and Fe_2O_3 .

2.3.1 Solar to Hydrogen Efficiency

The generally accepted solar-to-hydrogen (STH) efficiency target is ca. 10 %. The goal is to compete with the closest technological competitor: photovoltaic cells coupled to electrolyser, as highlighted e.g. by a US Department of Energy report [11, 15]. The ca. 10 % efficiency goal is based on multiplying the efficiencies of a typical PV cell and a typical electrolyser. For electrolysis, 1.6 V is a typical practical potential difference, and 1.23 V is the reversible potential difference, giving an (voltage) efficiency of 77 % (1.23 V/1.6 V). A typical commercial PV module efficiency is on the order of 15 % (electrical power output to solar power input). A photo-electrochemical device would need to meet this efficiency at the same or lower cost to be competitive with PV/electrolysis as a reference technology. The voltage of 1.23 V is the reversible potential for water splitting. Practical devices require higher voltages, as discussed further below.

As an example, a STH of 10 % efficiency for a typical solar flux, P_{solar} , of 1000 W m^{-2} corresponds to a photocurrent of 8.13 mA cm^{-2} or 81.3 A m^{-2} . This is based on the ratio of Gibbs free energy of the hydrogen ($\Delta G^\circ = -237.178 \text{ kJ mol}^{-1}$) generated at a rate R_{H_2} to the incoming solar irradiance [11, 16]. It also assumes zero external bias applied to the cell. The STH efficiency is given by Eq. (2.1).

$$\text{STH } \% = \Delta G^\circ R_{\text{H}_2} / P_{\text{solar}} \text{Area}_{\text{cell}} \quad (2.1)$$

Given that the production of each Mole of H_2 is directly related to the current, this is equivalent to:

$$\text{STH } \% = 1.23 J_{\text{photo}} \quad (2.2)$$

where J_{photo} is the photocurrent density. As each H_2 molecule requires two electrons (see hydrogen evolution reaction, Chap. 3 Eq. 3.2), the molar production rate is $R_{H_2} = j_{photo}/2F$, where F is the Faraday constant ($F = 96,485 \text{ C mol}^{-1}$), the charge on N_{Av} electrons [14, 16]. At 10 % STH this corresponds to quantities of about $150 \mu\text{mol h}^{-1} \text{ cm}^{-2}$ of hydrogen and $75 \mu\text{mol h}^{-1} \text{ cm}^{-2}$ of oxygen, as the ratio of production rates should be 2:1 according to the overall water splitting reaction.



A photo-anode needs to approach these efficiency values (or have the potential to) to be considered viable. However, few studies report their results in such a manner that the STH efficiency can be established, due to uncertainties of sample size, illumination intensity, and applied external bias.

2.3.1.1 Efficiency Limits

The main efficiency losses at various stages of solar water splitting, from initial photon absorption to the production of hydrogen, can be categorized as follows [14, 17]:

- Absorption of photons—how much of the solar spectrum that can be absorbed is limited by a material's band gap;
- Thermalisation of electrons as the energy of photons in excess of the band gap energy is lost by interaction with the lattice;
- Recombination of charge carriers in the bulk, at surfaces, and traps;
- Overpotential of electrons/holes—excess potential not utilised, but dissipated as heat;
- Resistive losses—due to resistivity of materials, interfaces, and electrolyte.

Osterloh et al. [17] noted that a single photocatalytic material device has a theoretical limit of less than 10 %—principally due to issues of bandgap, overpotential and the Shockley-Queisser limit, which is based on radiative, recombinative, and spectral losses. The overpotential required for a significant H_2 production rate is suggested to be about 0.6 V (0.3 V each for reduction and oxidation), giving 1.83 V as a minimum practical band gap and practical potential difference [9, 17]. A tandem device is more flexible as it adds the potential of two cells in series, but again the limit is of the order of 15 % from the need to absorb twice as many photons per electron. Multi-junction devices have reached efficiencies approaching 16 % through the use of multiple layers with graded band gaps [9, 18]. In both tandem and multi-junction devices, the top layer material has the highest bandgap, with each subsequent layer or cell having a smaller bandgap. For example, a top-cell made of TiO_2 could absorb UV light, and a bottom-cell made of Fe_2O_3 could absorb visible light. In multi-junction cells, the efficiency increases with the number of junctions.

2.4 Materials: Metal Oxides for Water Splitting

The materials TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ (for comparison) are now discussed in the context of the main material requirements for efficient water splitting as previously outlined. General material properties such as physical and electronic structure, or synthesis methods are not discussed here. These can be found in a range of reports [18, 19]. The basic requirements for water splitting can then be borne in mind when reviewing the effect of “plasmonic” metal nanoparticles in later sections.

2.4.1 Bandgap and the Solar Spectrum

The fundamental property of a semiconductor for solar cell applications is its bandgap. The generally accepted values of the indirect band gaps for rutile and anatase TiO_2 are 3.0 and 3.2 eV respectively [19, 20]. In terms of the wavelength of a photon, this corresponds to 413 and 388 nm. By comparison, the band gap of $\alpha\text{-Fe}_2\text{O}_3$ is in the region of 2.0–2.2 eV (620–564 nm) depending on material preparation [12, 20]. This immediately gives an upper limit to the efficiency of a solar cell. Figure 2.2 shows the standard Air Mass 1.5 solar spectrum used by the solar cell industry for terrestrial systems and shows how the 1000 W m^{-2} irradiance is distributed over the range of photon wavelengths.

A modified version of the spectrum in Fig. 2.2 shows the proportion of total energy in the solar spectra from photons of energy equal to, or greater than the bandgap of a material. The range of band gaps for TiO_2 and Fe_2O_3 are shown.

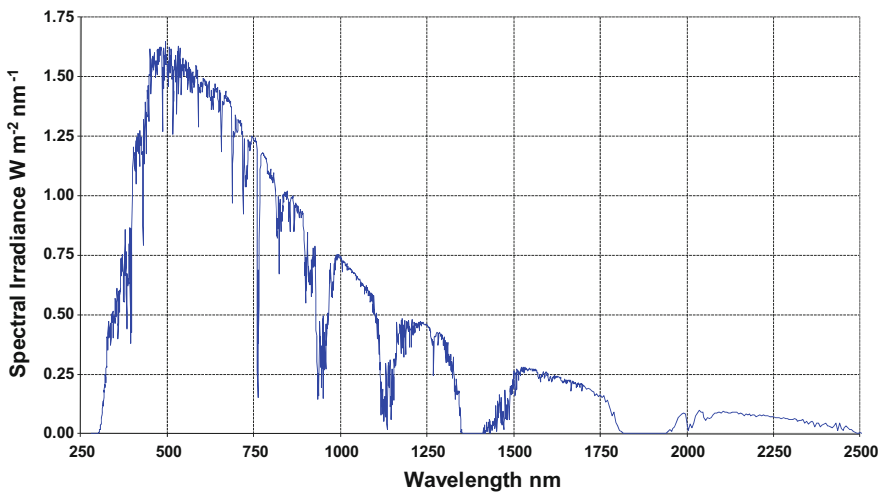


Fig. 2.2 Standard solar reference spectra—ASTM G173-03 (2012) used for solar cell design

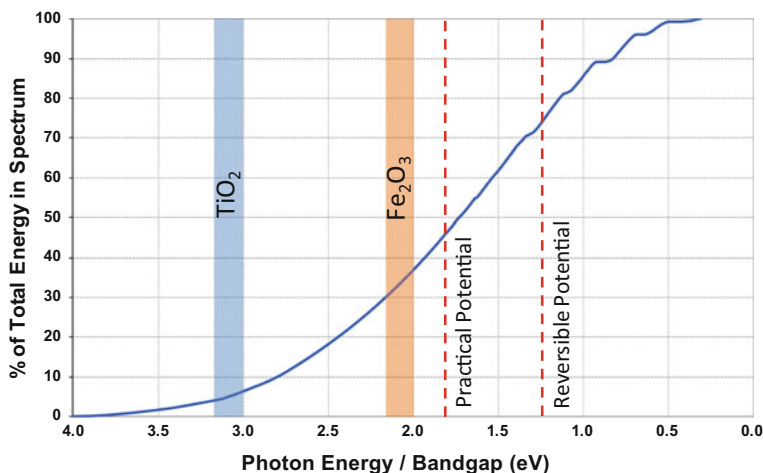


Fig. 2.3 Modified reference spectra showing cumulative solar energy with decreasing bandgap. The band gaps of TiO_2 and Fe_2O_3 are shown along with the reversible potential for water splitting and a practical potential

Based on Fig. 2.3 the maximum percentage of absorbable solar energy is between 4–6 % for TiO_2 , and 30–40 % for $\alpha\text{-Fe}_2\text{O}_3$. Taking thermalisation, recombination and resistive losses into account, the actual efficiency will be much lower. For TiO_2 , it is clear that 10 % STH efficiency is unachievable unless it is used alongside another material or sensitized to photons into the visible range (400–700 nm), for example with a light absorbing dye as in a dye-sensitized solar cell (DSSC), in which electrons are injected into the TiO_2 by the dye. The efficiency of a TiO_2 based DSSC is above 10 % indicating the potential for moderately high efficiencies with sensitized TiO_2 [12, 21]. However, this system is not suitable for direct water splitting, as it uses a regenerative redox couple such as $\text{Fe}^{3+}|\text{Fe}^{2+}$. It has also been proposed that a visible light absorbing metal nanoparticle (NP) could reproduce the same effect [21, 22]. Whether or not a metal NP system with TiO_2 is suitable for water splitting is one of the main areas of research of this thesis and is discussed in greater detail in the following sections. In the case of Fe_2O_3 , the band gap is ideal, but as discussed below the positions of the band edges are not. Additionally, Fe_2O_3 has been reported to have relatively poor charge transport characteristics [22, 23].

2.4.2 Band Position

The band structures of TiO_2 and Fe_2O_3 are discussed in terms of the general band structure requirements for water splitting.

Xu and Schoonen [23, 24] compiled a comprehensive list of the band positions of oxides based on experimental flat band data and calculation. Both TiO_2 and Fe_2O_3 have valence band edges significantly positive of the oxidation potential of water, so they should both sustain the oxygen evolution reaction (OER) under illumination. The conduction band of TiO_2 is just positive of the H^+/H_2 redox potential, suggesting that reduction of H^+/water and therefore unbiased water splitting is not possible. The position of the TiO_2 conduction band is sometimes reported as being slightly negative [24, 25]. This may be due to differences between anatase and rutile and other factors such as particle size and the surface of the material studied.

Fe_2O_3 also has a conduction band that is too positive to reduce H^+/water , so while it can absorb a greater proportion of the solar spectrum, it requires a significant bias in a hydrogen-producing PEC. The need to input energy decreases the achievable STH efficiency. Cesar et al. [25, 26] used two series-connected TiO_2 based DSSCs in a tandem cell configuration with a Fe_2O_3 anode to achieve water splitting estimated at 2.1 % STH efficiency from purely solar sources. This is a relatively high efficiency for a metal oxide based PEC. However, using three cells together in a system is complex and unlikely to be economic.

It is noted that another metal oxide, SrTiO_3 , with a bandgap of 3.2 eV (the same as anatase TiO_2) is the only oxide to have demonstrated full water splitting at zero bias [23, 26]. This can be attributed to the position of the conduction band being sufficiently negative of the reduction potential of water. As with TiO_2 , the large bandgap severely limits efficiency. However, it could offer a more promising starting material than TiO_2 , as it removes the need for bias. Nevertheless, the focus of this thesis is on aspects of TiO_2 related to water splitting.

In Fig. 2.4, the calculated conduction and valence band edges of a range of metal oxides are given, relative to the reduction and oxidation energies of water at pH 0. The data for TiO_2 and Fe_2O_3 are highlighted.

2.4.3 *TiO_2 and Fe_2O_3 for Water Splitting*

The first use of TiO_2 for photo-electrochemical water splitting is generally credited to Fujishima and Honda, who used a (001) rutile single crystal [27, 28]. Earlier work by Boddy, occasionally referenced, was an electrochemical investigation of TiO_2 only [11, 28, 29].

There have since been numerous reports of water splitting by TiO_2 studying effects of doping, particle size, synthesis and more. All have in common an extremely low STH efficiency, usually $\ll 1$ %. Many comprehensive reviews are available [11, 29, 30]. While the internal quantum efficiency of TiO_2 photo-anodes may be improved, the STH conversion efficiency is fundamentally limited by the large bandgap to well below an economical level. These studies in just TiO_2 are not

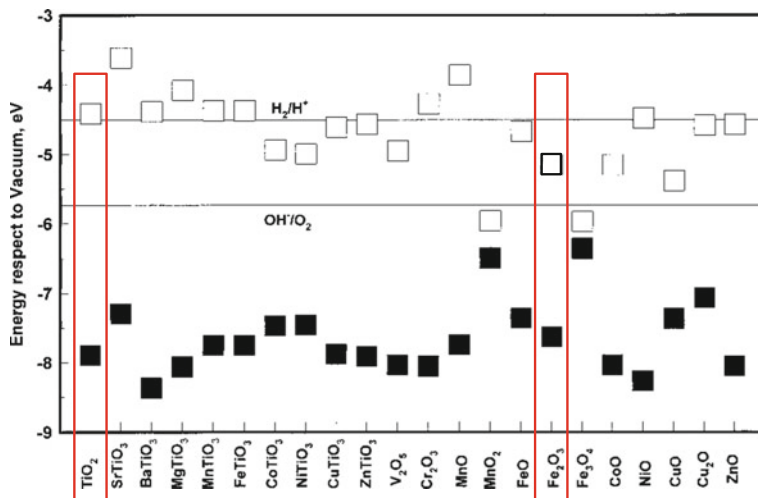


Fig. 2.4 Calculated energy positions (versus vacuum) of the conduction and valence band edges at pH 0 for selected metal oxide semiconductors. Taken from Xu and Schoonen [23, 27]. Reprinted with permission from Mineralogical Society of America

elaborated on here. The focus will be on systems functionalized with metal nanoparticles as a far less studied topic.

Neither TiO_2 nor Fe_2O_3 alone are suitable for achieving efficient water splitting; both require some bias or need to be used together in a tandem cell. However, they are worth studying as they are already fairly well documented and can be used as starting materials for modelling, to understand the various aspects of interesting surface phenomena, such as plasmonically-enhanced water splitting.

2.4.4 Other Water Splitting Materials

While TiO_2 is the focus of this thesis, there are numerous other possible materials for water splitting, such as SrTiO_3 as mentioned in Sect. 2.4.2. Tungsten trioxide (WO_3), which is stable in acidic solutions, is another well-known metal oxide and has even been used with Fe_2O_3 to improve charge separation by formation of a heterojunction [30, 31].

Oxynitrides are also being investigated as a potential materials group, due to the less positive position of their valence band. The nitrogen $2p$ orbitals are less negative (versus SHE) than the O orbitals, decreasing the band gap of the oxynitride compared to the metal-oxide. Essentially, this decreases the bandgap, allowing a greater proportion of the solar spectrum to be absorbed, which seems to be a promising avenue of investigation, although efficiencies remain low [22, 31].

2.4.5 Improving Solar to Hydrogen Efficiency

One approach to achieve increased efficiency of water splitting, while still using the cheap and stable material TiO_2 , might be sensitization to visible light: increasing how much of the energy in the spectrum is absorbed. As mentioned previously, dyes may achieve this, but would need to be developed to be stable in aqueous solution and resistant to oxidation. Another alternative, explored in this thesis is the use of surface plasmonic resonance on metal (gold) nanoparticles to absorb visible light. The general principle behind light absorption by metal NPs is outlined briefly below, followed by a review of key publications on TiO_2/Au systems used for solar energy, water splitting, and other redox reactions. The $\text{Fe}_2\text{O}_3/\text{Au}$ system has also been investigated [12, 22], but so far there is little in the literature on this combination, particularly for water splitting.

2.5 Plasmonic Water Splitting

The general idea of plasmonic photocurrent is that the addition of metal nanoparticles that support localized surface plasmon resonance (LSPR) can lead to the absorption of parts of the solar spectrum that the substrate material does not absorb. This is analogous to the dye-sensitization of TiO_2 in DSSCs [12, 32, 33]. Using a noble metal particle such as gold as the sensitizer may result in a more stable system in the oxidizing environment required for oxygen evolution in water splitting, as it is harder to oxidize gold compared to an organic dye. The intention in loading TiO_2 with gold nanoparticles is to extend the photocurrent generation of a TiO_2 based photo-electrochemical cell (PEC) from the UV into the visible region of the solar spectrum. The basic principle is illustrated in Fig. 2.5. In more detail, the concept of plasmonic enhancement of TiO_2 is as follows.

Titanium dioxide absorbs only UV light ($\lambda < 400$ nm), which makes up only 5 % of the energy in the solar spectrum. The majority lies in the visible and infrared part of the spectrum ($\lambda > 400$ nm). A gold nanoparticle demonstrating localized surface plasmon resonance will interact strongly with visible light, scattering and

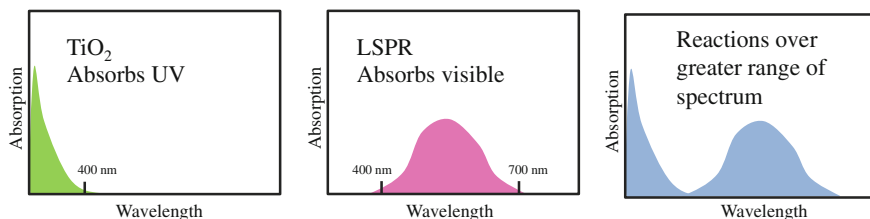


Fig. 2.5 Principle of using LSPR on a metal nanoparticle to extend the absorption of TiO_2 into the visible spectrum

absorbing around the resonant energy of the plasmon. The target is that the AuNP–TiO₂ system would therefore result in absorption of light from a larger portion of the spectrum. This is shown schematically in Fig. 2.5. Furthermore, it is hoped that the AuNP and TiO₂ will couple favourably and produce a photocurrent, enhanced relative to the TiO₂ alone, that will drive chemical reactions such as the oxidation of water.

In fact, enhanced photocurrents with visible light have been observed experimentally. Although, in most cases, the photocurrents generated at visible wavelengths of light are negligible. Any photocurrent generated at visible wavelengths corresponding to the LSPR, that cannot be attributed to the substrate material (TiO₂) is referred to in this thesis as ‘plasmonic photocurrent’. The term ‘plasmonic enhancement’ is often used in the literature. But this phrase is suggestive of the enhancement of a pre-existing photocurrent by the action of the plasmon. The phenomena of interest here is the generation of a photocurrent that is not possible for TiO₂ alone, due to the energy of photons being insufficient to generate electron-hole pairs, i.e. sub-band gap photons. Hence, the use of ‘plasmonic photocurrent’ in this thesis to distinguish the effects from each other.

This section examines the literature of ‘plasmonic enhancement’ and ‘plasmonic photocurrent’ of titanium dioxide by metal nanoparticles for photo-electrochemical water splitting. The focus is on studies with gold nanoparticles rather than silver as the plasmon resonance of silver is in the UV region of the spectrum, while the resonance of gold is in the visible. As the aim is to sensitize the TiO₂ to visible light, silver is not considered suitable. Furthermore, silver will rapidly oxidize in aqueous solution. The review covers existing studies of metal nanoparticles on TiO₂ and includes a critical discussion of the possible physical mechanism that could lead to an enhancement of performance. While the review is focussed primarily on water splitting for hydrogen production, other photo-electrochemical and photocatalytic applications are also discussed, as this is a relatively new area. Selected studies based on silver rather than gold nanoparticles are also discussed when relevant. The review concludes with suggestions for a course of investigation, which formed the results reported in this thesis.

Increasing the efficiency of metal NP and TiO₂ systems in practice will be dependent on being able to optimize the processes at work. To optimize a process requires a precise understanding of the mechanism at work, which is yet to be determined unambiguously. It is possible that once identified, the theoretical limit of efficiency may prove to be too low to indicate economic viability. At present, most studies have shown either no or negligible plasmonic photocurrent. Others show a negative impact overall. To date, the only reports known to the author that indicate a real plasmonic water splitting photocurrent with real-world potential are those by Nishijima et al. and by Tatsuma’s group [21, 32–35]. These studies have some interesting results that were not fully discussed by the authors. The studies are reviewed critically and in detail. A significant body of work by the Tatsuma group [21, 34–36] also suggested that TiO₂ loaded with plasmonically active gold nanoparticles can give good visible light performance in a PEC.

One of the main objectives of this thesis was to gain an understanding of the mechanism of plasmonic water splitting and to use this to fabricate photo-anodes that could be used to test and optimize the process. Hence, the critical review of the mechanisms presented in the literature.

The various proposed mechanisms discussed in detail during the course of this chapter are:

- ‘Hot’ electron injection or direct electron transfer (DET)
- Plasmonic Resonant Energy Transfer (PRET);
- Local heating
- Various effects of the ‘near-field’ around the nanoparticle (of which PRET could be considered one)

The following sections introduce plasmonic effects on nanoparticles, studies on water splitting and other photo-electrochemical systems involving plasmonic enhanced TiO_2 , and a critical discussion of the mechanisms that may be operative.

2.6 Plasmonic Nanoparticle Arrays

Illuminated metal nanoparticles (NP) may exhibit Localized Surface Plasmon Resonance (LSPR): oscillations of the electron plasma about the ion cores that affect the absorption and scattering of light. The electric field around the nanoparticles is also concentrated due to the small size of the nanoparticles: the ‘lightning-rod’ effect. The electric field local to the nanoparticle is often referred to as the ‘near-field’ [36]. The effect of the electric field of incident light on the electrons in the nanoparticle is shown schematically in Fig. 2.6. The action of the electric field (denoted by E) causes the electrons at the surface of the metal nanoparticle to oscillate relative to the positive ions of the metal atoms. The electrons oscillate collectively at the frequency of the incident photon, resulting in

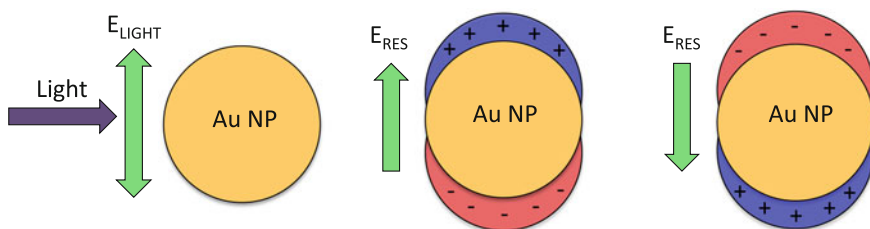


Fig. 2.6 Oscillation of electrons in a metal nanoparticle due to oscillating electric field of incident light, E_{LIGHT} results in electric field of localized surface plasmon resonance E_{RES} [36, 38]

positive and negative poles on the surface of the nanoparticle. For a spherical nanoparticle, a dipole is formed with an electric field E_{RES} . For other geometries (rectangles, triangles), multiple poles are possible [37].

For nanoparticles deposited on a substrate, there can also be a plasmonic effect at the interface called a Surface Plasmon Polariton (SPP). This is a wave that travels along the interface, and that can be used as a waveguide. The effect of the near-field of both LSPs and SPPs on the substrate is unknown. It may alter the absorption or band structure of the supporting material, it may influence charge separation or transfer, or have little effect.

Systems incorporating ‘plasmonic’ metal nanoparticles and semiconductors have been investigated as a means to improve the efficiency of both photovoltaic (PV) and photo-electrochemical cells. While the mechanisms behind the enhancement of PV, such as increased path length due to scattering [38, 39] and increased coupling of light into the substrate [39, 40] are reasonably well understood, the effects in photo-electrochemical and photocatalytic systems including TiO_2 are not.

The detailed theory of plasmonics is available from many sources [36, 40–42], but is not presented here. The focus of this review is not on how a plasmon is excited, or modelling the absorption, but on the effect in photo-electrochemical systems.

Studies have shown that the number of resonances, resonant wavelengths, and intensity of plasmonic resonance is highly dependent on the size and shape of the nanoparticle, as well as the refractive index of the environment [32, 36, 41, 42]. It is reasonable to suppose that metal nanoparticle arrays of gold or other metals may be designed to absorb light optimally at any wavelength or range of wavelengths desired, such as the solar spectrum. These arrays can be fabricated on suitable TiO_2 substrates. What is unknown is how to design the Au- TiO_2 system as a whole, to optimize the generation of photocurrent under visible light.

2.7 TiO_2 -AuNP Systems for Water Splitting

The key results of several studies of AuNP enhanced TiO_2 are presented below. While not all are related to the photo-electrolysis of water, they are informative for this thesis. Nishijima’s study [32, 33] is introduced first, as it is both the most relevant and the most interesting, and formed a starting point for the work described in Chap. 5 of this thesis. Other studies are introduced as necessary to aid discussion of issues such as the effect of phase (rutile or anatase), doping, nanoparticle array architecture, and applications. Finally, the proposed mechanisms are discussed in the light of these studies and other ‘plasmonic’ photo-electrochemical studies involving different oxides and applications.

2.7.1 Nishijima et al. [32, 33]

Nishijima et al. [32, 33, 42] investigated photo-anodes comprised of arrays of Au nano-rods (AuNRs) and nano-discs (AuNDs) on niobium doped (0.05 % by weight) rutile single crystals with a (110) orientation. The study reports incident current to photon efficiencies (IPCE) of 5–10 % at the peaks, and internal quantum efficiencies (IQE) of 10–15 %. To our knowledge, these figures are orders of magnitude higher than any others reported for the Au-TiO₂ system. The authors suggest that injection of hot electrons from the AuNR/AuND into the conduction band of the TiO₂ is responsible for the photocurrent.

The nanostructures were deposited by electron-beam lithography, which allows precise control over size and shape, but is limited to coverage of small areas: 1 mm² in this instance. The AuNRs were 110 × 240 nm² and AuNDs were 125 × 125 nm² as shown in Fig. 2.7. Both sets of structures were 40 nm thick with a 2 nm Ti layer between the gold and TiO₂, which is a typical approach used to improve the adhesion of gold to a substrate in physical vapour deposition. The more recent of the two studies by the same authors uses AuNRs of similar dimensions. For the AuNRs, the UV-Vis-NIR extinction spectra (Fig. 2.8a, black line) demonstrated two peaks, at 650 nm and 1000 nm, which are attributed to LSPR on the short and long axes of the rods. Light polarized transversely or longitudinally with respect to the AuNRs showed only one of the peaks (Fig. 2.8a, red and blue lines). It is noted that this measurement was of extinction, which included absorption and scattering/reflection. However, the symmetric AuNDs displayed

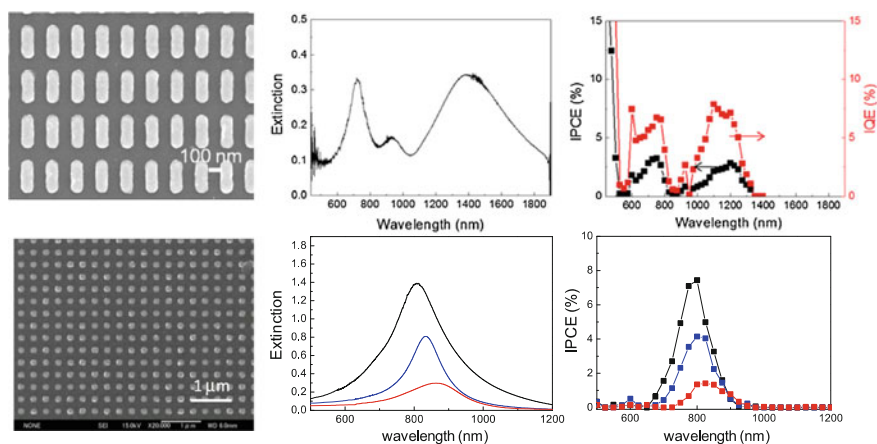


Fig. 2.7 Results of the studies by Nishijima et al. [32, 42]. The *top row* shows the characteristics of nano-rods, while the *bottom row* shows nano-discs. The *left-hand panels* are SEM images, the *central panel* is the optical extinction, and the *right-hand panel* is the incident-photon-to-current-efficiency (IPCE). The curves in the *bottom row* correspond to varying separation of the nano-discs. Reprinted (adapted) with permission from Nishijima et al. [32]. Copyright (2010), American Chemical Society

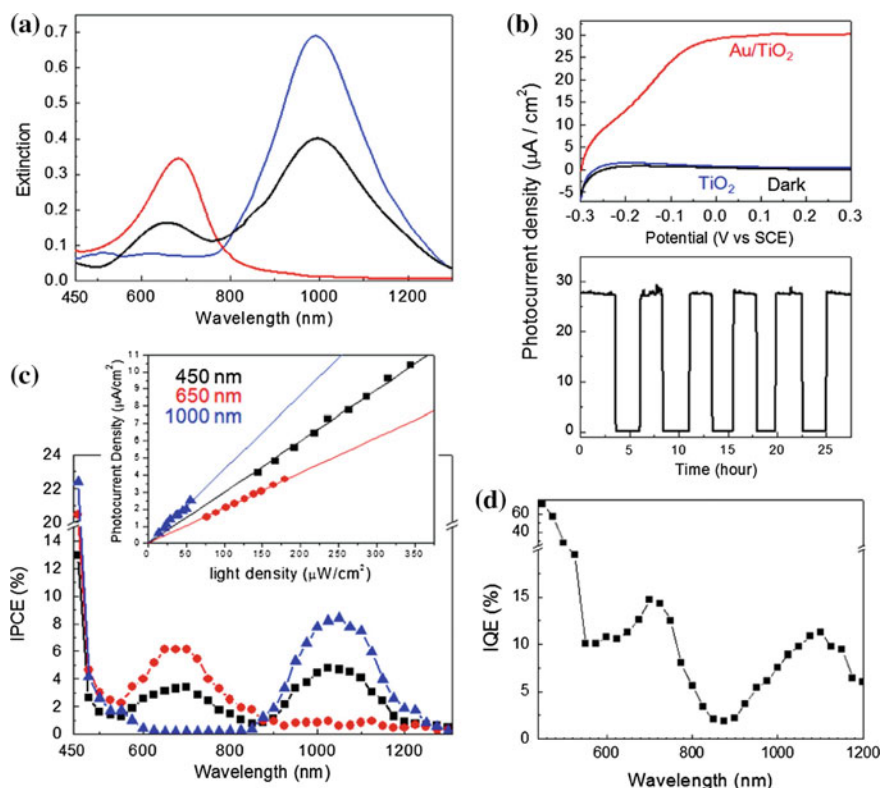


Fig. 2.8 Results of the study by Nishijima et al. [33] reproduced directly from the paper. Panel **a** shows the extinction spectra for the nano-rods with polarized (red and blue lines) and unpolarized light (black). Panel **b** shows the photocurrent for the Au/TiO₂ (red line, black line without illumination) and bare TiO₂ (blue line). Panels **c** and **d** show the IPCE and IQE (internal quantum efficiency). Reprinted (adapted) with permission from (Nishijima et al. [32]. Copyright (2010) American Chemical Society

only a single extinction peak, the position of which varied between 800 and 850 nm, depending on how densely packed the array was, demonstrating plasmonic coupling between nanoparticles [32, 42].

The most compelling aspect of this work is that a significant photocurrent (an IPCE above 5 % at visible wavelengths) is reported at visible and NIR wavelengths, as shown in the rightmost panel of Fig. 2.7 and in Fig. 2.8c. Photocurrent measurements in monochromatic light show a response that matches the extinction spectra closely. There is a slight shift in the position of both the visible and the near-infra-red (NIR) peak. This could be attributed to the fact that the resonance for absorption and scattering in LSPR on a metal nanoparticle may occur at slightly different wavelengths [33, 42]. Monochromatic light was used with a cut-off filter to remove any residual UV to ensure that all current measured was attributable to visible light. This was identified as a potential issue during the work reported in this

thesis; a monochromator can produce higher order harmonics. For example, light monochromated to 700 nm can have a 350 nm component, which will directly excite electron-hole pairs in TiO₂ leading to spurious results. The type of cut-off filter used in the reviewed publication was not identified.

Under illumination by 500–1300 nm light (of unspecified intensity), a photocurrent of 30 $\mu\text{A cm}^{-2}$ was achieved. On illumination by monochromatic light at 450, 650, and 1000 nm wavelengths, there appeared to be a linear increase of photocurrent with increasing intensity (inset in Fig. 2.8c). Illumination intensity varied from 10–350 $\mu\text{W cm}^{-2}$, resulting in photocurrents of up to 10 $\mu\text{A cm}^{-2}$. As presented, the measured photocurrent seemed to increase with photon energy; the intensity of the shorter wavelength light was higher.

In the insert of Fig. 2.8c, extrapolated linear fits of the photocurrent for 450, 600, and 1000 nm light indicates that a higher photocurrent could be produced by the lowest energy photons. If this is a process with an energy threshold, then it is reasonable, as the 1000 nm incident beam would contain more photons per Watt per unit area. However, the 650 nm illumination produced a lower current than the 450 nm, which is not congruous with a simple picture of an energy threshold. The authors of the study did not make these observations.

Furthermore, it is noted in this thesis that a photocurrent is generated at photon energies below the reversible energy for water splitting of 1.23 eV, which is equivalent to a wavelength of 1008 nm. This might indicate that the energy of multiple photons is required to produce the observed photocurrent.

The experiment was carried out in water at pH 7 with a 100 mM KClO₄, with a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The photocurrent onset seemed to start at -0.3 V and incident photon charge carrier efficiency (IPCE) measurements were made at $+0.3$ V (SCE), which corresponded respectively to -0.056 and 0.544 V versus SHE (based on SCE being $+0.245$ V vs. SHE). At pH 7, the equilibrium potentials for hydrogen and oxygen are at -0.413 V (SHE) and $+0.817$ V, respectively. Measurements were also made in KCl with 1×10^{-3} mol dm⁻³ of 1,2-benzenediol as an electron donor, resulting in photocurrents greater by a factor of 1.4. The equilibrium potential of 1,2-benzenediol (presumably oxidized to CO₂) was given as $+0.32$ V (SHE), which is much less positive than that for oxidation of water. Such a small increase is somewhat surprising given the usual exponential effect of increasing overpotential, unless adsorbed reactants and products inhibited reaction rates.

It was also noted by Nishijima et al. that the photovoltage of the AuNR patterned sample increased compared to that of the bare(un-patterned) TiO₂, which could indicate more free electrons in the conduction band, due to increased absorption of light. The authors attribute the detected current to the oxidation of water, suggesting the possibility of utilizing visible light in a water splitting system based on TiO₂. This was confirmed in their later study by detection of generated hydrogen and oxygen by gas chromatography—mass spectroscopy (GS–MS) [33, 43].

One detail that is not mentioned in the paper is the optical extinction spectra of the bare TiO₂ substrate. While the doping level of the TiO₂ substrate with Nb was only 0.05 wt%, this would have resulted in significant absorption in the visible and

IR spectrum compared to undoped single crystal TiO_2 , as found in attempts to reproduce the result of this paper and discussed in Chap. 5.

Based on this result, it seems to be possible to oxidize water efficiently with visible light using gold nanoparticles on TiO_2 , specifically if using 0.05 wt% Nb-doped rutile (110). Whether the effect can occur with other crystallographic orientations, dopants and doping levels, or on other phases like anatase is undetermined. The following reviews of papers try to address these questions. It is noted that the authors of the study did not discuss whether or not the doping of the TiO_2 substrate was an important feature.

2.7.2 Liu et al. (2011)

Liu et al. [43, 44] also studied plasmonic enhancement of water splitting using gold nanoparticles on TiO_2 . The study was based on anatase TiO_2 nanotubes formed by anodizing Ti foil in a NH_4F electrolyte (Fig. 2.9). Then 5 nm of Au was deposited using electron beam evaporation, which formed densely packed islands rather than a continuous film. The authors highlighted a decrease in photocurrent under UV light, due to the dense gold film preventing light from reaching the TiO_2 .

Under illumination by monochromated light, there is a twofold enhancement of photocurrent at 532 nm and a peak enhancement of sevenfold near 650 nm (Fig. 2.9f). However, these enhancements are of a small photocurrent density of the order of hundreds of nano-amperes (not given as a current density, Fig. 2.9e. In this

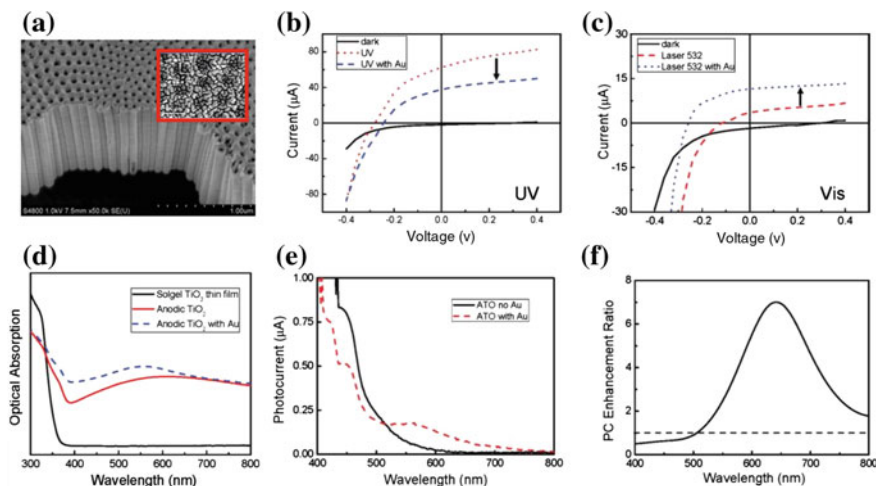


Fig. 2.9 Effect of gold nanoparticle film (*inset*) on anatase TiO_2 nanotubes under UV light (b) and visible illumination (c). Absorption, photocurrent over the visible part of the spectrum and the enhancement ratio are shown in (d), (e), and (f). Reprinted with permission from Liu et al. [43]. Copyright 2010 American Chemical Society

case, the plasmonic effect may have been an enhancement of a pre-existing photocurrent or the dark current. What is clear is that the TiO₂ nano-tube film had significant absorption of visible light compared to un-doped TiO₂ synthesized by a sol-gel process, which was explained by accidental doping by N and F present in the electrolyte during the anodizing process (Fig. 2.9d).

Repeating the photocurrent experiment with a sol-gel TiO₂ film (presumably also anatase) rather than anodized Ti gave no photocurrent under visible light, either with or without gold particles. The authors suggested that enhancement of absorption by nanotube films due to their doping was responsible, rather than injection of electrons, which they argued should have occurred with both the sol-gel film and the nanotube film. This conclusion suggested that doping could also have been responsible for the photocurrent reported in Nishijima's paper, based on Nb-doped TiO₂ having significant absorption in visible light (see Chap. 5 of this thesis).

The two studies introduced so far showed that it may be possible to use TiO₂ with gold nanoparticles to split water using visible light. However, it is equally possible to fabricate materials that decrease the overall efficiency of the system.

2.7.3 *Naseri et al. (2010)*

Naseri et al. [44, 45] studied anatase TiO₂ films loaded with AuNPs that exhibited visible light absorption due to SPR, resulting in doubling of photocurrents with Au present, but of magnitudes less than 0.4 A m^{-2} , which corresponded to a STH efficiency of $<0.5 \%$ under 0.1 W cm^{-2} light or 4 A W^{-1} . This was attributed to (assumed rather than measured) water splitting in the visible part of the spectrum. It was not clear whether the source spectra included UV light, so it is hard to confirm whether photocurrents were due to visible light absorption or UV.

2.7.4 *Chandrasekharan and Kamat (2000)*

Chandrasekharan and Kamat [45] authored the earliest paper reporting attempts to exploit visible light absorption of AuNPs to enhance the photo-electrochemical performance of TiO₂. They did not discuss water splitting, nor assigned reactions, nor identified a redox couple explicitly, but as they used 0.05 M NaOH electrolyte, it is assumed that no other redox species were added. The TiO₂ was produced by a sol-gel process, followed by annealing at 400 °C, which should have produced an anatase film, although this was not characterised. The gold nanoparticles were formed by immersing the electrode in a toluene solution containing 5 nm gold colloids that adsorbed onto the TiO₂ film surface and aggregating as 20–70 nm clusters (Fig. 2.10). The Au/TiO₂ film exhibited a SPR at 546 nm (red-shifted from Mie Theory), but the spectral response of photocurrents was shown not to be

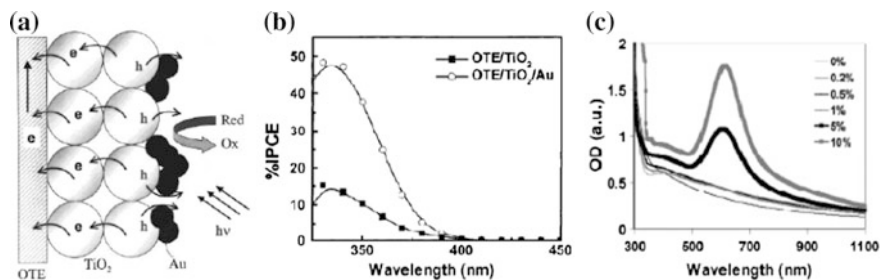
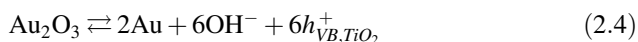


Fig. 2.10 Effect of gold nanoparticles on photocurrent of TiO₂ PEC. Schematic diagram of Au nanoparticles on TiO₂ film (a), measured photocurrent (b), and film absorbance (c) [43, 45]. Reprinted with permission from Chandrasekharan et al. [45]. Copyright 2000 American Chemical Society

influenced by the addition of the Au particles, i.e. there was no photocurrent response to visible light. However, photocurrents were enhanced threefold and the photovoltage also increased. It was suggested that the AuNPs increased charge transfer rates between the TiO₂ and electrolyte by decreasing overpotentials. While the catalytic process was not identified, an example might be Au₂O₃/Au(OH)₃, formed by hole-driven oxidation following photon absorption by TiO₂, acting as a catalyst for water/OH⁻ oxidation:



where,

$$E_{\text{Au}_2\text{O}_3/\text{Au}}(\text{SHE})/V = 1.363 - 0.0592 \text{ pH} \quad (2.5)$$

Another possibility is that the nanoparticles scattered the incident UV light, increasing the optical path length of the material, so increasing rates of electron-hole pair generation.

Based on the small photocurrent densities reported by Liu et al. [21, 43] and the results in Chap. 5 of this thesis, it is possible that there was a small visible light photocurrent present in the study by Chandrasekharan and Kamat, but that it was not detected. As the following studies by the Tatsuma group showed, it is possible to have a measurable and significant plasmonic enhancement of photo-electrochemical reaction rates on anatase TiO₂.

2.7.5 Tatsuma Group

Tatsuma's group at the University of Tokyo, Japan, have reported several studies of the photo-electrochemistry of Au-TiO₂ systems. Though not necessarily all for

aqueous solutions, they are critically reviewed for this thesis when relevant information was identified.

Tian and Tatsuma [21] investigated nano-porous anatase TiO₂ films loaded with Au or Ag nanoparticles in a photo-electrochemical cell with aqueous 0.05 M NaOH solution and also with an I⁻/I₃⁻ couple for measurement short-circuit currents. The I⁻/I₃⁻ couple was likely used due to being more thermodynamically and kinetically facile than oxidizing hydroxide ions to oxygen. The redox potential also sits between the conduction and valence bands, permitting the reaction to occur without additional bias. The application of bias would render the short circuit current meaningless. An anatase precursor sol was spin-coated onto ITO and annealed at 500 °C. The resulting anatase film was then immersed in an ethanol solution containing Au colloids of 5–20 nm diameter to coat the surface with Au particles. The Au coated TiO₂ exhibited LSPR at 542 nm, which was red-shifted from the 530 nm of the colloidal solution, due to the higher refractive index of the TiO₂ substrate. The response of the system to monochromatic light from 400 to 700 nm followed the absorption/extinction spectra closely (Fig. 2.11). There was a

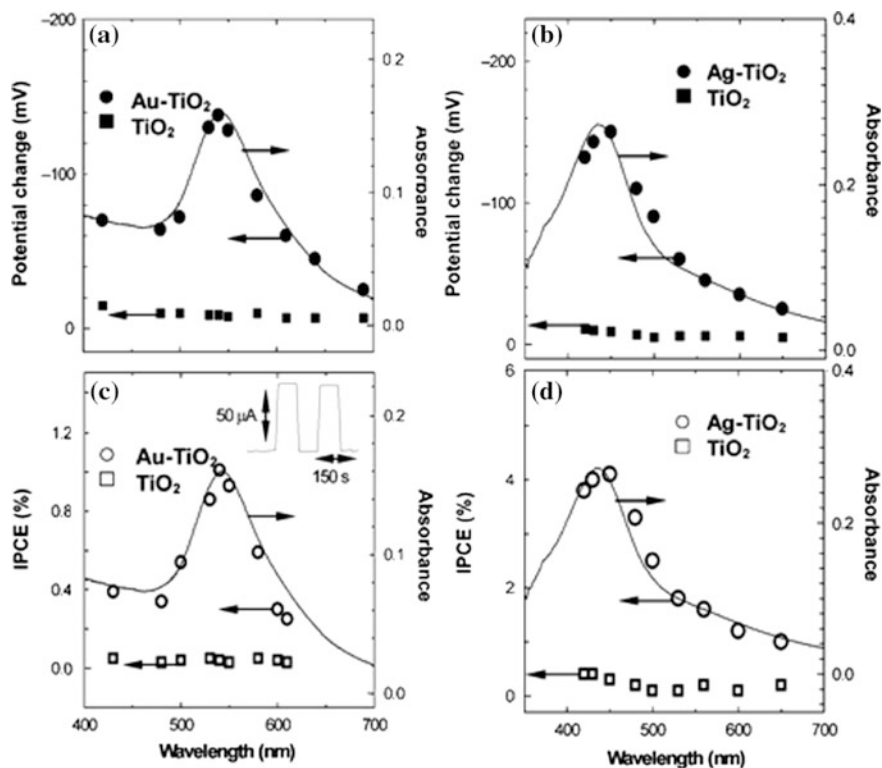


Fig. 2.11 Results reported by Tian and Tatsuma [21, 34]. The open circuit potential and IPCE are shown against the absorbance for both gold- (left-hand images) and silver- (right-hand images) NP coated anatase TiO₂. Reprinted (adapted) with permission. Copyright © 2004, Royal Society of Chemistry

measurable short-circuit current under illumination that peaked at 1 % IPCE at 540 nm. Likewise, the open circuit potential became more negative in the presence of the gold, peaking at -140 mV relative to that of bare TiO_2 . A similar behaviour was seen with silver nanoparticles in place of gold.

The authors described this behaviour as ‘remarkable’ and attributed the effect to the plasmon absorption of the gold nanoparticles. They proposed that the electric field in the TiO_2 space charge layer influenced the oscillating electrons in the metal nanoparticles, drawing the electrons into the conduction band of the TiO_2 substrate, and leaving positively charged metal nanoparticles that oxidized hydroxide ions to oxygen.

Tian and Tatsuma [34, 45] continued the work by investigating the effect of changing the redox couples, noting that the system with I^- as an electron donor was not entirely stable. TiO_2 films of $4\text{ }\mu\text{m}$ thickness were obtained by spin coated sol-gel. In contrast to the previous work, the gold nanoparticles were formed by photocatalytic reduction. Films were immersed in $5 \times 10^{-3}\text{ mol dm}^{-3}$ of HAuCl_4 for 30 min and then irradiated with UV light to form $<50\text{ nm}$ diameter nanoparticles. The most promising redox couple tested was $\text{Fe}^{2+}|\text{Fe}^{3+}$, with the optimum ratio of FeCl_2 – FeCl_3 identified to be 0.1 and 0.05 M, respectively, in a solution of N_2 -saturated acetonitrile and ethylene glycol in a 60/40 volume ratio. An IPCE of 12 % at a wavelength of 560 nm was reported, corresponding to an energy conversion efficiency of 1.27 % with illumination of 10 mW cm^{-2} . With the addition of 0.2 M 4-nitrobenzoic acid, the IPCE increased up to 26 %. Methanol, ethanol and other hydrocarbons were also investigated to establish the feasibility of a ‘photovoltaic fuel cell’, but the IPCE was found to be much lower, perhaps due to gold being a poor alcohol oxidation catalyst. It was also seen that the presence of O_2 , a by-product of the oxidation, decreased the IPCE efficiencies. The solution was found to contain H_2O_2 , which is a product of O_2 reduction, suggesting that the O_2 accepts electrons from either the gold and/or TiO_2 , decreasing the number reaching the cathode, and the efficiencies of the circuit.

While this is not a water splitting application, it shows that an anatase TiO_2 -Au system can be driven by visible light to do useful work. It also highlights the potential problem of simultaneous O_2 reduction at an O_2 evolving photo-anode. In a water splitting cell, this unwanted side-reaction would decrease the electron concentration available for hydrogen production.

2.8 Mechanisms of Plasmonic Enhancement

It is apparent from the literature that there are uncertainties as to the processes leading to plasmonic enhancement of photo-electrochemical reactions or generation of plasmonically-induced visible light photocurrent. Several common explanations are presented below and are discussed critically. Reports on plasmonic enhancement of both TiO_2 and other metal oxides and semiconductors are considered. The phenomenon of interest is how the Au- TiO_2 system can produce photocurrent under

visible light. Increased photocurrent at UV wavelengths, at which TiO_2 is already photoactive, as seen by Chandrasekharan and Kamat [12, 45], is not considered in detail.

2.8.1 Direct Electron Transfer (DET)

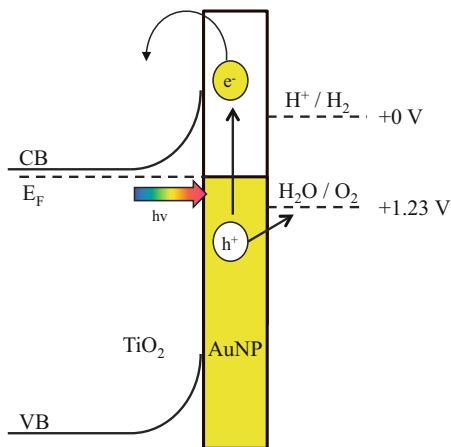
The most common mechanism proposed in the literature is that of electron injection also referred to as direct electron transfer (DET), which is proposed to act in a similar manner as dye-sensitized solar cells [12, 34]. The originators of this mechanism appear to be Tian and Tatsuma [32, 34]. They propose that:

1. A photon is absorbed by a surface plasmon on a metal nanoparticle;
2. Electrons in the metal nanoparticle oscillate close to the interface with the TiO_2 ;
3. The electric field in the space charge layer of the TiO_2 causes electrons in the metal nanoparticle to be injected into the TiO_2 conduction band;
4. The positively charged metal nanoparticle oxidizes the electron donor in solution.

The suggested steps in the process are illustrated schematically in Fig. 2.12. The effect of the plasmon is to give an electron sufficient energy to overcome the Schottky barrier at the interface between Au and TiO_2 .

Nishijima et al. [32, 33] also proposed the injection of an electron as the principal mechanism in a water splitting process, although they do note that there may also be some non-linear effects due to the electric field enhancement operative. They suggested that an electron is promoted from the filled d-band of the AuNP into the conduction band of TiO_2 , followed by electron donation from H_2O to the AuNP to compensate the electron loss. In more recent papers [33, 46], they expanded on this concept. Later, the authors considered the requirement for a hole

Fig. 2.12 Schematic of electron injection from a metal nanoparticle into the conduction band of TiO_2



to drive the oxidation. It was noted that for water oxidation to occur, four holes of sufficient potential are required for each molecule of oxygen. They suggested that the injection of electrons from the gold would leave a net positive charge on the metal nanoparticle that oxidizes H_2O or OH^- and that the positive charge could be considered as a de-localized hole at the surface.

The suggestion of a positively charged hole in a metal could be considered controversial. The electronic structure of metals is conventionally described in terms of the free electron gas [46–48]. To suggest that there is a long-lived hole with a defined energy and sufficient potential to accept an electron is a novel and unproven concept. However, Petek et al. [47–49] have measured the generation of electron-hole pairs in metals such as gold and copper at ultrafast timescales. While an extremely short-lived hole may be possible, it is not certain whether it is possible for these holes to have a sufficient lifetime to accept an electron from a solution species. Typically, the hole is filled by a cascade of electrons from higher to lower energies within the nanoparticle, for example by Auger recombination. This is also unlikely given the typical femtosecond timescale (10^{15} Hz) of the plasmon oscillation. Furthermore, the potential of any hole is undetermined, but would have to be positive of the water oxidation potential.

On the physical scale of energy, and at pH 0, water reduction occurs at about -4.5 eV (versus vacuum), and oxidation at -5.73 eV. The work function of gold is around 5.4 eV [49, 50]. Converting to the absolute potential scale, this suggests that the Fermi level of gold at $+0.9$ V (SHE) is not positive enough to oxidize water, which is at $+1.23$ V (SHE). If the work function of gold is unaffected by pH (and adsorbed ions), then the potentials of water oxidation and the Fermi level of gold become equal at pH 5.6. At pH 5.6 and above, it should be possible for water to be oxidized by a hole at the potential of the Fermi level. However, if the gold is in nanoparticle form, it might be possible that the potential of the TiO_2 substrate determines the potential of the Fermi level of gold.

Details of how the injection of the electron into the TiO_2 might proceed are also uncertain. Nishijima et al. proposed the electron is excited from the d-band to the s, p band in gold, and is then swept into the TiO_2 . Again, this suggests a long-lived excitation in the gold nanoparticle, as if it were a molecule with discrete energy levels. This may be possible with gold nanoparticles below 10 nm [51]. This is clearly not the case for the Nishijima study.

Recent papers suggest that surface plasmons can indeed decay into ‘hot electrons’. These are electrons with an excess of energy above the Fermi level. Giugni et al. [50, 52] demonstrated the conversion of SPPs on the tip of a gold plasmonic waveguide to hot electrons with an apparent efficiency of 30% . The hot electrons were injected across the Schottky barrier formed between the gold tip and GaAs. The authors noted that the decay of a plasmon into a hot electron, rather than radiative decay (scattering), might be enhanced by a rough Schottky barrier contact. This might explain why larger nanoparticles (such as those fabricated by Nishijima et al.) perform well, due to the increased likelihood of defects in the contact area.

Further studies have suggested that plasmons decay into ‘hot electrons’. Knight et al. [52, 53] detected photocurrents from arrays of AuNPs deposited on Si, with

photocurrents corresponding to the absorption of photons with energies smaller than the band gap of Si. This was attributed to hot electron transfer into the semiconductor. Mubeen et al. [53, 54] coated AuNRs with TiO_2 , Pt for water reduction and a Co oxidation catalyst. They observed both hydrogen and oxygen evolution under visible light, and attributed this to hot electron transfer. The results of experiments by Mukherjee et al. suggested that these hot electrons can also transfer into a Feshbach resonance of hydrogen molecules on gold nanoparticles, causing the dissociation of H_2 into atomic hydrogen [54, 55].

How the hot electrons are generated by the decay of the surface plasmon is not clear at this stage, and is only speculated. It could be hypothesized that an electron oscillating around the ionic core due to an applied electric field has increased potential and kinetic energies (forced-damped harmonic oscillation), which could raise the potential of some electrons above the Fermi level, to an energy at which they can be injected into the conduction band by the electrostatic field, or by tunnelling. This picture of a distribution of electron energies, above the usual Fermi-level, was used by Cushing et al. [55, 56] in their investigation of the photocurrent enhancement mechanism of Cu_2O films loaded with gold nanoparticles. The plasmonic photocurrent was attributed to a plasmonic resonant energy transfer (PRET, discussed in Sect. 2.8.2) mechanism between the Au and Cu_2O . However, follow up papers on Ag- Cu_2O core-shell structures by the same authors [52, 53, 56], reported a mixture of behaviour that was attributed to both PRET and DET, depending on the wavelength of the incident light.

In a talk at the Materials Research Society Spring 2013 symposium, Peter Nordlander² suggested that, rather than decaying to a distribution of energies, the plasmon may decay into a single hot electron with energy above the Fermi level of the metal equal to the energy of the exciting photon (no discussion was given regarding the generation of a hole). Given that a surface plasmon is often visualized as the collective oscillation of all free electrons at the surface of a nanoparticle, it is surprising that, rather than a distribution of energies, that the energy should be transferred to a single electron.

Recently, Sundararaman et al. [57] predicted the decay of plasmons and generation of both hot electrons and hot holes in metals by means of a quantized plasmon model and electronic states calculated with density functional theory (DFT). The authors predict a distribution of hot electrons above the Fermi level and a distribution of holes below the Fermi level. This appears to be an important step in beginning to explain how a plasmon can decay and result in the reduction or oxidation of a species in solution. Manjavacas et al. [58] have also estimated hot carrier generation using Fermi's Golden Rule. Govorov et al. [59] have investigated, theoretically, the injection of hot electrons from metal nanoparticles into semiconductor substrates by quantum mechanical methods. Overall, it appears that direct electron injection is beginning to develop a theoretical basis to support the observations of experimental work.

²To the knowledge of the author of this thesis, there has not been a related publication.

A number of studies [52, 53] suggest that the emission of hot electrons follows the Fowler formula (a form of which is given in Eq. (2.6)). The proposal is that the rate of photoelectrons with sufficient energy to overcome the Schottky barrier is given by a relation of the form:

$$g = C_f \frac{(h\nu - \phi_{SB})^n}{h\nu} \quad (2.6)$$

where g is a generation rate of electrons, C_f is the Fowler emission coefficient, $n = 2$ for most metals, and ϕ_{SB} , the Schottky barrier height. The study by Mubeen et al. [53] claimed that this equation fits data well. When the current increased at wavelengths corresponding to plasmonic resonance, the divergence from the above fit was attributed to an enhancement due to the plasmonic resonance [52, 60].

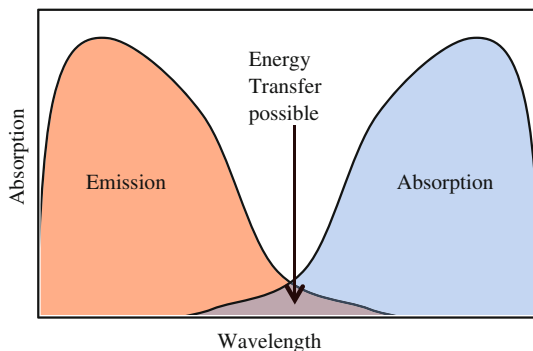
At energies above the plasmonic resonance, the photocurrent should be ascribed to the usual generation of electron-hole pairs, not hot electrons. Over the region of the plasmonic resonance, the fit of Eq. (2.6) to a typical current-potential curve for plasmonic enhancement is poor. At lower energies, the fit clearly diverges from the data, so while the fit follows the general trend, it is suggested here that the fit does not capture the effects of the plasmon resonance.

To accurately fit the plasmonic photocurrent data reported in this thesis, the Fowler Eq. (2.6) as presented above would need to be modified to account for the plasmonic enhancement, perhaps in the scaling constant C_f . It could be hypothesized that, based on equations for thermionic emission as presented by Murphy and Good [61] and Fowler and Nordheim and others [62, 63], the effect of the plasmon resonance is similar to either the temperature term of the electric field term. Greater photon energy is analogous to higher temperature. However, as the photocurrent has a maximum at a particular energy, rather than simply increasing with photon energy, it may be better to formulate this in terms of the electric (near) field, which is maximized at the plasmon resonance and may be high at the surface of a nanoparticle.

2.8.2 Plasmonic Resonant Energy Transfer (PRET)

Resonant Energy Transfer (RET) involves coupling between dipoles of two materials such as a nanoparticle and a molecule or nanowire of different materials by Coulomb forces. This can allow efficient energy transfer from one material to another, say between nanoparticles [64, 65] or from a plasmon to a fluorescent molecule. However, it is noted that the materials must have similar response to excitation, suggesting that an excitation produced by visible-light in one material cannot couple to a material with a significantly larger energy requirement for excitation. For example it is noted that ZnO and TiO₂ can couple to enhance fluorescence [64, 66] and also CdTe with plasmons in Au [66, 67]. Cascading from high to low energy is also seen from ZnO to an organic molecule via FRET;

Fig. 2.13 Schematic of energy transfer between two materials, in which transfer is possible only if the absorption spectrum (blue) of the receiving material overlaps the emission spectrum (red) of the material emitting the photon



however, the reverse is not seen [67–70]. Whether this dipole oscillation energy transfer is possible for a plasmonic TiO_2 system requires further investigation, as a standard TiO_2 excitation is far from that of an Au nanoparticle.

The theoretical foundations of resonant energy transfer has been described by Andrews [55, 68–70], who showed that both Resonant Energy Transfer (RET) and inverse-square radiation were the near-field and far-field asymptotic solutions of energy exchange by emission of photons. In both cases, energy transfer is possible only if there is an overlap of the emission and absorption spectra of the emitter and absorber, as shown in Fig. 2.13. In the case of near-field energy transfer, often referred to as Förster Resonant Energy Transfer (FRET), the energy transfer is by exchange of virtual photons, while in the far field the exchange occurs through a real photon.

Energy transfer from the decay of a surface plasmon to the excitation of an electron-hole pair in a semiconductor could be viewed as a form of resonant energy transfer, and has been referred to as Plasmonic Resonant Energy Transfer (PRET). The study by Cushing et al. [55] used the effect of an insulating SiO_2 spacer layer between the Ag and Cu_2O to demonstrate that energy transfer occurs even when the gold nanoparticle and Cu_2O are separated. It is noted here that the band gap of Cu_2O (ca. 2.2 eV) coincides with the resonant wavelength of AuNPs.

A standard formulation of resonant energy transfer [55] is given without proof to demonstrate the fundamental requirement for overlapping emission and absorption spectra:

$$w_{FRET} = \frac{9\kappa^2 c^2}{8\pi\tau_{A*} n^4 R^6} \int \frac{F_A(\omega)\sigma_B(\omega)}{\omega^4} d\omega \quad (2.7)$$

where, the rate of transfer w_{FRET} depends on the product of the emission $F_A(\omega)$ and the absorption $\sigma_B(\omega)$ at each frequency ω . The transition rate decreases as R^{-6} , where R is the distance between particles. If there is no overlap, the integral is zero, and the rate of energy transfer is zero. The remaining parameters are related to the material.

Cushing et al. [22, 55] estimated an emission/absorption rate for a plasmonic metal nanoparticle based on the dipole moment of the localized surface plasmon (LSPR) given by Mie theory. The requirement for overlapping absorption of nanoparticle and semiconductor was also highlighted in a recent study by Thimsen et al. [22] of AuNPs with Fe_2O_3 for water splitting. Two architectures were investigated: fully embedded particles and surface deposition. It was clear that the AuNPs improved the magnitude of absorbance in both cases. The effect of the hematite dielectric environment was to red-shift the plasmon resonance from 550 nm to about 650 nm, resulting in less overlap with the Fe_2O_3 absorption and less probability of energy transfer. While there was increased absorbance for the embedded architecture, there was only a slight improvement in the photocurrent of the embedded system at high bias. This suggested that even with an emission and absorption overlap, it is not a simple matter that the addition of metal nanoparticles will improve performance. For the surface configuration, the overall effect under AM1.5 light was negative. The authors attributed this to the formation of Schottky barriers between Au and Fe_2O_3 , resulting in lower open circuit potentials than the standard Fe_2O_3 - H_2O junction. They speculated that increasing the Schottky barrier height might help overcome this drawback, although do not elaborate on the reasoning.

Given the large band gap of both rutile (3.05 eV) and anatase (3.2 eV) TiO_2 , it seems that resonant energy transfer from a visible light absorbing surface plasmon to TiO_2 would occur with an extremely low probability. The only way this would be likely is if multiple plasmons could decay simultaneously and pool their energy into exciting an electron hole pair in TiO_2 . The concept of energy pooling has been touched on by Andrews [70] as being a real process, but there has been no proposal that this may be in effect for the Au- TiO_2 system.

For energy pooling to occur, it seems to the author of this thesis that the surface plasmons of adjacent nanoparticles should be coupled. This is more likely to occur if the nanoparticles are of uniform size, shape, and separation and are separated by a distance of less than the wavelength of the plasmon. This may explain why the nanoparticle array used by Nishijima et al. [32] performed so well. The paper also demonstrated (in the supplementary information) that the efficiency of the process was dependent on the inter-particle spacing.

2.9 Other Plasmonic Effects

2.9.1 *Effect of Enhanced Near-Field on Absorption*

In addition to DET and RET, another suggestion for the mechanism of plasmonic enhancement is the effect of the enhanced electric field at the surface of a metal nanoparticle supporting a surface plasmon. Liu et al. [43] note that doping materials can reduce the bandgap and allow absorption of visible light. They suggested that

the electric near-field formed at the surface of the nanoparticle creates an enhancement of the electric field at the interface of the AuNP and TiO₂ surface that influences charge separation and suppresses recombination, resulting in higher photocurrent. Nishijima et al. [32] also indicated that they believed there was a non-linear effect due to the enhanced electric field, in addition to electron injection, but do not expand.

It is not unreasonable to suggest that a larger electric field could enhance photocurrent generation. From Fermi's Golden rule [71], the transition rate is dependent on the square of the Hamiltonian operating on the initial and final states. Cushing et al. [55] derived a form for the transition rate in a semiconductor (2.8) that demonstrates that the rate of photon absorption, or transition rate w_{SEMI} , is proportional to the intensity of the electric field $|E_0|^2$ (the square of the field strength E_0) and as such an enhanced field should result in more electron-hole pairs, and subsequently higher photocurrent densities. The other terms are not defined here as the equation is only presented to highlight the $|E_0|^2$ dependence.

$$w_{SEMI} = \frac{e^2 |E_0|^2}{4\pi^2 m^2 \hbar \omega^2} |p_0|^2 \left(\frac{2m_{reduced}}{\hbar^2} \right)^{3/2} (\hbar\omega - E_G)^{1/2} \quad (2.8)$$

This argument may be true at a particular point local to a nanoparticle, but over a large area, the incoming photon flux is fixed, so the total absorption should remain constant. The effect of the enhanced electric field should be to increase the absorption coefficient, resulting in a shorter absorption depth for a given material. Exactly how the enhanced field might decrease recombination rates, as suggested by Liu et al. [43], is not clear.

Furthermore, the effect of enhancing the absorption coefficient of a material relies on that material absorbing at the plasmon resonance. For a material like TiO₂, if the photons are of below band gap energy, then enhancing the electric field cannot cause the absorption of a photon. This is shown by the term $(\hbar\omega - E_G)^{1/2}$, which only evaluates for $\hbar\omega > E_G$. However, for above band gap energy photons, it would be possible to enhance the absorption coefficient.

For these reasons, it is suggested here that enhanced absorption due to the intensification of the electric field at the surface of a metal nanoparticle cannot be the driving mechanism for the plasmonic photocurrent in Au-TiO₂ photo-anodes, as there is no overlap of the absorption spectrum of TiO₂ with the emission of gold nanoparticles in the visible spectrum.

2.10 Evidence for Direct Electron Transfer

Several sets of data are now examined that support direct electron transfer (DET) as the mechanism of plasmonic photocurrent for the Au-TiO₂ system.

2.10.1 Electrons in the Conduction Band of TiO_2

Furube et al. [72] have demonstrated that DET might take place using femtosecond transient absorption spectroscopy (TAS). They compared TiO_2 films with embedded AuNPs to films with a light absorbing ruthenium based “N-3” dye, as used in dye-sensitized solar cells (DSSCs), in which electron injection is known to occur from the dye to the TiO_2 . The absorbance of a 3500 nm IR probe by electrons in the TiO_2 conduction band was measured. The system was excited by a 550 nm laser i.e. by photons with insufficient energy to directly excite electron-hole pairs in the TiO_2 . Figure 2.14 shows the transient absorbance of 3500 nm light by conduction band electrons following the 550 nm excitation. The absorbance of the Au/TiO_2 system under pulsed excitation was similar to the N3 dye/ TiO_2 system, although the lifetime of the excitation was shorter lived, decaying after about 1 ns. The authors inferred that this implies that electrons were injected into the TiO_2 from the AuNP, as in the dye system.

It is suggested here that the TAS measurements are not conclusive evidence of DET. While they do demonstrate the presence of electrons in the conduction band of TiO_2 following illumination with visible light, they do not give any indication of the origin of the electrons. It is inferred by the authors of the study that because the dye injects electrons, that the gold nanoparticle must also do so. It is possible that the electrons are excited directly from the valence band of the TiO_2 somehow. A possible experiment to verify this would be a TAS measurement probing for holes rather than electrons. If a population of holes are measured in the valence band of TiO_2 , then it might indicate that the electrons originate within the TiO_2 , while the absence of the hole signal would support DET.

The fact that the effect is not seen with ZrO_2 is attributed by the authors to the more negative potential of the conduction band of ZrO_2 compared to TiO_2 . This additional potential barrier might be sufficient to prevent the transfer of electrons. Likewise, if the conduction band electrons were generated in the TiO_2 itself, the larger band gap of ca. 5 eV could also prevent this from occurring in ZrO_2 .

Fig. 2.14 Transient absorbance of TiO_2 films loaded with dye and AuNPs, and Au-loaded ZrO_2 . Figure taken from publication [72]. Reprinted with permission from Furube et al. [72]. Copyright 2007 American Chemical Society

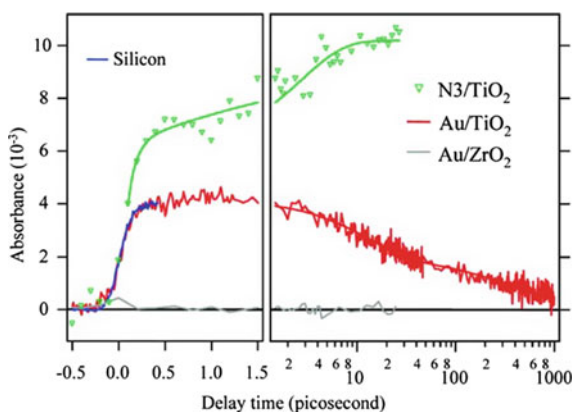


Fig. 2.15 Potential change of illuminated AuNP–TiO₂ electrode under monochromatic illumination. Figure taken from publication [21]. Reprinted (adapted) with permission. Copyright © 2004, Royal Society of Chemistry

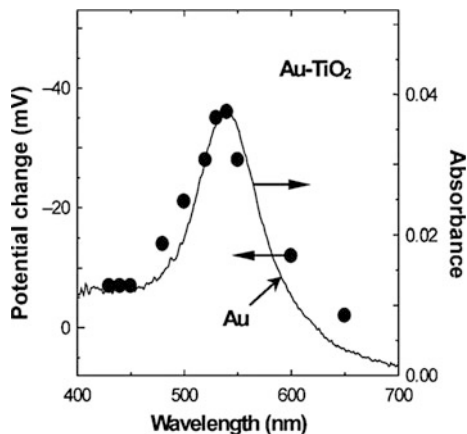
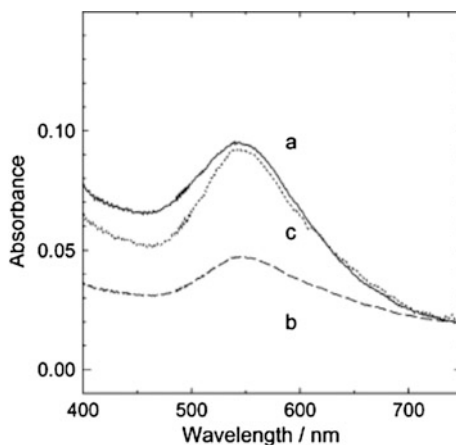


Fig. 2.16 Effect of extended period of illumination on the absorbance of Au–TiO₂ at open circuit (a), in the absence of an electron donor (b) and after the introduction of ethanol (c). Figure taken from publication [21]. Reprinted with permission from Tian et al. [21]. Copyright 2005 American Chemical Society



Two other sets of data used to support the DET mechanism were identified by Tian and Tatsuma [21, 34]. The first was the negative shift in open circuit potential (seemingly versus $\text{Fe}^{3+}/\text{Fe}^{2+}$) under visible light illumination (Fig. 2.15). The second was the decreased absorbance of the gold nanoparticles following extended illumination in white light, which was reversed by addition of an electron donor, such as ethanol (Fig. 2.16).

2.10.2 Shifting Open Circuit Potential Under Illumination

A negative shift in the open circuit potential under monochromatic illumination was detected in the anatase AuNP–TiO₂ systems studied by Tian and Tatsuma [21] (Fig. 2.15) and supports DET. In a conventional PEC, illuminating the junction

generates electron-hole pairs and splits the quasi-Fermi levels. This allows current to flow and un-bends the bands, resulting in a negative shift in the open circuit potential of the electrode. Tian and Tatsuma saw a similar shift of potential on illumination of their AuNP-TiO₂ system by visible light in multiple experiments. The shift in potential was attributed to the presence of electrons in the conduction band of TiO₂. As the photons are not energetic enough to promote these electrons from the valence band, it was inferred that the electrons must have come from the metal. As with the TAS measurements discussed previously, it could be said that while this measurement shows there are electrons in the conduction band, it does not show an absence of holes. If the effect of the plasmon resonance on the gold nanoparticle was generating electron-hole pairs in the TiO₂ by some other unknown mechanism, then the same negative potential shift would be expected; this measurement cannot in itself distinguish between electron transfer from Au and electron-hole pair generation in TiO₂. As shown in Fig. 2.15 the potential change follows the absorbance of the plasmon, with the largest shift at the plasmon resonance. This suggests that the number of electrons in the conduction band was directly related to the strength of the excitation of the nanoparticles.

2.10.3 *Decrease in Absorbance of Plasmon*

Tian and Tatsuma also investigated the effect of an electron donor on the absorbance around the surface plasmon resonance. Following irradiation with visible light for 30 min at 10 mW cm⁻², the absorbance (presumably measured in terms of transmittance) was decreased (Fig. 2.16). The decreased absorbance was attributed to loss of electrons from the gold nanoparticle, due to the excitation of electrons and injection into the TiO₂. Adding 0.5 M ethanol as an electron donor resulted in the recovery of the absorbance peak. It was suggested that this regenerated the electrons in the gold nanoparticles. It was not made clear by the authors whether the Au-TiO₂ sample was immersed in water only with no control of the electrode potential.

On this basis, it might be imagined that without the addition of an electron donor, the gold nanoparticle would become depleted of electrons to the point that the absorption of light and photocurrent decreases and stops. This in turn would suggest that a system for producing hydrogen by water splitting would not be practical, as it would require a sacrificial electron donor.

The standard equilibrium potential of CO₂/ethanol is -0.346 V (SHE) at pH 7, compared to +0.817 V (SHE) for water oxidation [73]. The Fermi level of gold should be at a potential of +0.6 to +0.9 V (SHE) based on the vacuum level being at -4.5 V on the SHE scale and the work function of gold being between 5.1 and 5.4 eV. This suggests that electrons could be donated by ethanol easily, but not by water at this pH. For water to act as an electron donor to gold, the oxidation potential of water should be less positive than the potential of the gold. This will depend on both the pH and the work function of the gold nanoparticle, indicating

that an investigation of the dependence of photocurrent on pH might be prudent for Au-TiO₂ systems.

The preceding paragraphs discussed the evidence for and against DET the main candidate for the plasmonic photocurrent mechanism. Generally, the evidence for Au-TiO₂ systems allows for the possibility of DET. The TAS and negative potential shift measurements are considered compatible with DET, but do not rule out any other possibilities.

2.10.4 Opposition to DET Mechanism

Liu et al. [43] refute the DET explanation, stressing that electron excitation in metals and dyes are not comparable, because in a dye molecule, there is a long-lived excitation and electron-hole pair generation, which has not been observed in gold nanoparticles. Control studies using sol gel films and ITO as the substrate for the gold nano-island film did not exhibit any visible light photocurrent. The authors reasoned that if DET was the mechanism, then the effect should work with both the sol-gel film and the ITO, but as no effect was observed, there must be some other mechanism at work. The point regarding ITO may be discounted as ITO is essentially metallic by design, so would have had no extended depletion region and electric field to effect charge separation. Any electron transferred to the ITO may easily recombine with the AuNP. The lack of photocurrent from AuNPs on anatase films prepared by a sol-gel process followed by thermal treatment is in-line with the work of Chandrasekharan and Kamat [45], and Naseri [44]. However, the studies by Tian and Tatsuma [21, 34] showed that plasmonic photocurrent with anatase and AuNPs was indeed possible (but with redox couples other than water). The lack of enhancement could perhaps have been due to the nature of the gold nano-islands, which did not demonstrate a sharp peak of plasmon resonance in absorbance, and were in addition deposited only on the top of the film. By comparison, Tatsuma's films were nano-porous and loaded with gold nanoparticles exhibiting a well-defined resonance in the absorption spectrum. This suggests that both the interfacial area and/or the strength of the resonance and the associated electric field are important factors in producing charge transfer from the AuNP to the semiconductor.

Another possibility is that in the study by Liu et al. the depletion region of un-doped anatase was significantly wider than that of the anatase nano-tubular film, due to the N and F impurities in the nanotube film decreasing the strength of the field and efficiency of charge separation. However, this would probably also apply to the films of Tian and Tatsuma.

Furthermore, there is a feature of Nishijima's study [32] that also casts doubt on the DET theory. The general picture presented is that of electron transport by the action of the electric field at a Schottky barrier between gold and TiO₂. However, in their case, there was a 2 nm thick titanium layer between the gold and TiO₂, so that the TiO₂ should have formed an ohmic contact with the Ti. While there is only

2 nm of Ti, there should be sufficient charge carrier density in both the Au and Ti to compensate for the differences in Fermi levels (work functions) between the metals and the oxide. The differences in Fermi levels at the Ti–Au interface should not present a barrier to charge movement from Au to Ti or from Ti to TiO_2 . The Ti should have been screened the Au from the TiO_2 , unless the Au was determining the equilibrium potential. It is noted that in the study by Knight et al. [52] that there was also a Ti layer between the AuNRs and Si substrate. This too should have prevented the formation of a Schottky barrier between the Au and Si.

Of course, the systems studied by the Tatsuma group and other groups did not include a Ti interlayer, so they would form a Schottky barrier between the anatase TiO_2 and Au. This might indicate that either a different mechanism was at work in each and every case, or that a mechanism that is not dependent on the presence of a Schottky barrier is acting.

Where the TiO_2 is directly in contact with the electrolyte, however, there should be a semiconductor-liquid junction of the Schottky barrier type, in addition to a Schottky barrier or ohmic contact at the semiconductor-metal junction. This complicates the analysis and understanding of the system significantly and is beyond the scope of this review. Further information can be found elsewhere, such as in the chapter by Allongue, in *Modern Aspects of Electrochemistry* [74], which discusses the effect of metal-semiconductor junctions in electrochemistry.

This is not to say that DET could not be the active mechanism. But this critical review serves to highlight the fact that it has not yet been proven conclusively to be operative. A theory of plasmonic photocurrent that can be tested rigorously is presently lacking in the literature.

2.11 Oriented Thin Films of TiO_2

Surface modification of TiO_2 by gold nanoparticles has been reviewed previously. Another aspect of this thesis is to investigate the surface of TiO_2 itself.

As described in results Chaps. 7 and 8, part of the project required the growth of epitaxial thin films of TiO_2 with different orientations, principally rutile (110), anatase (101), (100), and (001). The films were to be used to study the dependence of water adsorption and charge transfer on specific features of these surfaces, and to help to validate the theoretical modelling part of the wider research programme. In particular, a parallel project under the same Programme Grant investigated the adsorption modes of water on the rutile (110) surface using density functional theory computations [75]. For anatase TiO_2 , water is also known to adsorb both molecularly and dissociatively, e.g. at oxygen bridging vacancies, depending on the polymorph and the surface exposed, in addition to factors such as temperature [76–78].

The focus of this section of the literature review is to identify a range of growth conditions to begin investigating how best to form the oriented thin films. Further publications are discussed in Chaps. 7 and 8 of this thesis reporting the growth of TiO_2 thin films by pulsed laser deposition (PLD).

The background to the need for oriented TiO_2 thin films is given in brief. It is possible to purchase high quality single crystal rutile substrates with a range of orientations including (100), (001), (110), and (011). These single crystals can also be doped with a range of other elements and can be grown using high temperature processes such as the Verneuil process. As such, it is relatively straightforward to obtain high quality ‘ideal’ surfaces to study and compare their properties and behaviour with computational predictions. In the case of anatase, it is not possible to grow high quality single crystals with control of the purity, as an anatase precursor would be required. To date only the synthesis of micron sized single crystals of anatase has been achieved [79]. It is likely that the high temperatures required to fuse, say an anatase powder, would result in a phase change from anatase to rutile, preventing the growth of millimetre scale single crystals. At present, most surface science studies of anatase single crystals have been carried out on naturally occurring samples of uncontrolled purity. An alternative approach is to grow epitaxial thin films of anatase on other single crystal substrates [80]. An advantage of growing anatase films is also the flexibility of doping the films during the growth process.

It is possible to deposit films of either the rutile or anatase morphology of TiO_2 , and with different crystallographic orientations, by changing either the substrate [81] and/or varying the deposition temperature and pressure [82]. The initial literature search concentrated on identifying a range of suitable substrates, which act as the growth template, for films with a range of low index orientations e.g. (100), (001), (101).

Silva et al. [81] investigated the growth of TiO_2 films on a range of cubic single crystal substrates, including MgO , LaAlO_3 , and SrTiO_3 , on which the films were grown by pulsed laser deposition (PLD) at an oxygen partial pressure of 10 Pa. The laser fluence was set to 2 J cm^{-2} with 2 Hz repetition rate, while the deposition temperature was varied. All films were deposited from a sintered rutile target. The advantage of PLD is the possibility of growing a low temperature phase from a high temperature phase target.

Silva et al. [81] found that on both LaAlO_3 (100) and SrTiO_3 (100), the films were anatase with a (001) orientation, i.e. the *a* and *b* axes of the unit cell grew in plane, with the *c* axis perpendicular to the interface of film and substrate. This was unsurprising, giving the close match of the *a/b* lattice parameters: 3.9050 Å for SrTiO_3 , 3.792 Å for LaAlO_3 , and 3.7852 Å for anatase. The ordering of the film on LaAlO_3 was seen to be better than the film on SrTiO_3 , due to the better lattice match with anatase. On MgO (100), the films grew as anatase (100), i.e. the anatase *c* axis was in the plane of the interface between the film and the substrate. The authors suggested an epitaxial relation for the anatase film on MgO , which the author of this thesis believes to be in error (see Chap. 8). The epitaxial relation of anatase to MgO is discussed in detail in Chap. 8 of this thesis.

The same authors also grew anatase (102) films on SrTiO_3 (110) and rutile (110) on MgO (110). Films grown on (110) $\bar{1}00$ M-plane sapphire were rutile (001); those grown on (0001) C-plane sapphire were a mixture of anatase and rutile, and

Table 2.1 Potential substrates and temperature for growth of oriented TiO₂ films by pulsed laser deposition

Orientation	Substrate	Temperature (K)	Reference
Rutile (110)	Glass/FTO MgO (110)	>873	Hitosugi et al. [83] Silva et al. [81]
Anatase (101)	Glass/FTO		Hitosugi et al. [83]
Anatase (100)	MgO (100)	<873	Silva et al. [81]
Anatase (001)	STO (100) LAO (100)	873 873	Silva et al. [81] Hsieh et al. [84]

those grown on (1102) R-plane sapphire were rutile (011). The study of Silva et al. also tabulates the results of numerous studies on the growth of epitaxial TiO₂ films on single crystals by a range of deposition methods.

Table 2.1 suggests some suitable substrates and conditions for TiO₂ thin films that were used as a starting point to produce oriented films of anatase (101), (100), and (001), which were of primary interest. The growth of anatase (101) films is discussed further in the following section.

It is also possible to grow epitaxial TiO₂ films on Si substrates using an intermediate buffer layer of SrTiO₃ or TiN prior to the deposition of TiO₂ [85–87].

It is also noted that certain surfaces of films are more likely to form than others, due to having a lower surface energy; e.g. rutile (110) and anatase (101) are most likely [88]. This can be seen in studies with films deposited on amorphous substrates, on which the films were amorphous on deposition and annealed thereafter; higher annealing temperatures resulted in rutile instead of anatase. These films are discussed further in the following section.

2.12 Conductive TiO₂ Thin Films

Growth of conductive TiO₂ thin films were investigated due to the interest in; making surface measurements, and using the thin films as electrodes. In both cases, the films would need to have a measure of conductivity to allow the current-voltage response to be established. Un-doped TiO₂ films are too resistive for use as electrodes and cannot be imaged by scanning tunnelling microscopy (STM).

Several publications have demonstrated that it is possible to grow crystalline anatase films with a (101) orientation on borosilicate glass [82, 83, 89–91]. The publications all stem from a group at the Kanagawa Academy of Science and Technology, Kawasaki, Japan. The group reported the growth of a transparent conducting oxide comprised of Nb-doped anatase TiO₂ [89]. The initial films were grown on SrTiO₃ single crystals, and demonstrated resistivity on the order of 10^{−3} Ω cm with doping by Nb of 1 % and above [89, 90]. The same authors grew Nb_{0.06}Ti_{0.94}O₂ films with the (101) orientation on borosilicate glass, and demonstrated that annealing the films in H₂ resulted in lower resistivity. They then

investigated the effect of growing the films at room temperature followed by annealing in H₂; films grown at room temperature were amorphous, but when annealed subsequently appeared to be more crystalline than the films grown at temperature. The films deposited at room temperature also appeared to be more uniform with a flat surface and an absence of visible grains compared to the films deposited at temperature.

The films grown on borosilicate glass appeared to be comprised of (101) oriented grains only. On this basis, borosilicate glass and fused silica was identified as potential substrates for the growth of (101) oriented films, as presented in Chap. 7 of this thesis.

The observation of conductivity in the Nb-doped anatase films was also promising, as it suggested that it would be possible to deposit conductive films that might be suitable for study by surface probe techniques, such as STM.

In this project, given the interest in Nb-doped TiO₂ for both the thin film deposition and as the substrate for the high performance plasmonic photocurrent generation reported by Nishijima et al. [34], a review of the defect chemistry of TiO₂ and Nb-doped TiO₂ was undertaken and is presented in Appendix A. This is discussed further in Chap. 7, which reports the growth of anatase films with Nb-doping. The effect of doping on the stability of anatase is also discussed. The reason for including the defect chemistry in such detail was that it was reviewed in detail to try to understand why TiO₂ films doped with Nb failed to demonstrate measurable levels of conductivity. Additionally, it was used to try to understand the differences between Nb-doped and reduced rutile, as reported in Chap. 6.

2.13 Summary of Literature Review

The preceding literature review focuses on two main areas: plasmonic Au-TiO₂ photo-anodes for solar water splitting, and to a lesser extent TiO₂ thin films and the defect chemistry of Nb-doped TiO₂.

The review of Au-TiO₂ was used to organize and contrast themes in the many studies regarding its use in photo-electrochemical cells. The purpose was to try to understand if the mechanism of plasmonic water splitting had been previously elucidated in the literature. Based on the current literature, it appears there are several mechanisms proposed, based on experimental observation, but no theoretical framework that adequately describes the process of that can be used to predict or analyse the performance of Au-TiO₂ photo-anodes. However, a paper published by Sundararaman et al. before final submission of this thesis appears to be beginning to develop a theoretical framework [57].

The review was also used to inform the choice of direction for the experimental work presented in Chaps. 5 and 6 of this thesis. Based on the work of Nishijima et al. rutile (110) single crystals doped with Nb were identified as a substrate capable, in principle, of high performance. The suggestion by Liu et al. that dopants

might be partly responsible led to the decision to compare Nb-doped and un-doped rutile (110) single crystals.

The review of TiO₂ thin films was used to identify initial growth conditions and substrates for pulsed laser deposition of thin films. The aim of the experimental work was to identify the particular conditions required in the apparatus available, rather than in general. As such, an exhaustive review of TiO₂ thin films was felt to be unnecessary. The focus of the work reported in Chaps. 7 and 8 was to map out the parameter space of the equipment.

The review of the defect chemistry of TiO₂ was carried out (and included here) as it provided useful information on the behaviour of both Nb-doped and reduced TiO₂, which is relevant to the work on both the Au-TiO₂ photo-anodes and the deposition of thin films.

In the following chapter, the principles of photo-electrochemical cells as applied to TiO₂ are covered in greater detail, and lead into the experimental methods used.

References

1. De-La-Rosa, Y.: World Population to 2300, pp. 1–254. United Nations Publications, NY (2004)
2. International Energy Agency: World Energy Outlook 2010 International Energy Agency, Paris (2010)
3. Solomon, S.: Climate Change 2007—The Physical Science Basis. Cambridge University Press, Cambridge (2007)
4. Britain, G.: Climate Change Act 2008. The Stationery Office, London (2008)
5. Boyle, G.: Renewable Energy. Oxford University Press, Oxford (2012)
6. Twidell, J. Weir, A.D. Renewable Energy Resources. Taylor & Francis, London (2006)
7. Larminie, J., Dicks, A.: Fuel Cell Systems Explained. Wiley, NY (2003)
8. Hoffmann, P.: Tomorrow's Energy. MIT Press, Cambridge (2012)
9. Khaselev, O., Bansal, A.: High-efficiency integrated multijunction photovoltaic/electrolysis systems for hydrogen production. *Int. J. Hydrogen Energy*. 1–6 (2000)
10. Pijpers, J.J., Winkler, M.T., Surendranath, Y., Buonassisi, T., Nocera, D.G.: Light-induced water oxidation at silicon electrodes functionalized with a cobalt oxygen-evolving catalyst. *Proc. Natl. Acad. Sci. U.S.A.* **108**, 10056–10061 (2011)
11. Vayssieres, L.: On Solar Hydrogen and Nanotechnology. Wiley, NY (2010)
12. Grätzel, M.: Photoelectrochemical cells. *Nature* **414**, 338–344 (2001)
13. Kudo, A.: Z-scheme photocatalyst systems for water splitting under visible light irradiation. *MRS Bull.* **36**, 32–38 (2011)
14. Rajeshwar, K., McConnell, R.D., Licht, S.: Solar Hydrogen Generation. Springer, New York (2008). doi:[10.1007/978-0-387-72810-0](https://doi.org/10.1007/978-0-387-72810-0)
15. Dresselhaus, M., Crabtree, G., Buchanan, M.: Basic Research Needs for the Hydrogen Economy. (2003)
16. Atkins, P., de Paula, J.: Atkins' Physical Chemistry. Oxford University Press, Oxford (2010)
17. Osterloh, F.E., Parkinson, B.A.: Recent developments in solar water-splitting photocatalysis. *MRS Bull.* **36**, 17–22 (2011)
18. Cronmeyer, D.C.: Electrical and optical properties of rutile single crystals. *Phys. Rev.* **87**, 876 (1952)
19. Diebold, U.: The surface science of titanium dioxide. *Surf. Sci. Rep.* **48**, 53–229 (2003)

20. Liao, P., Toroker, M.C., Carter, E.A.: Electron transport in pure and doped hematite. *Nano Lett.* **11**, 1775–1781 (2011)
21. Tian, Y., Tatsuma, T.: Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO_2 . *Chem. Commun.* 1810 (2004). doi:[10.1039/b405061d](https://doi.org/10.1039/b405061d)
22. Thimsen, E., Le Formal, F., Grätzel, M., Warren, S.C.: Influence of plasmonic Au nanoparticles on the photoactivity of Fe_2O_3 electrodes for water splitting. *Nano Lett.* **11**, 35–43 (2011)
23. Xu, Y., Schoonen, M.A.: The absolute energy positions of conduction and valence bands of selected semiconducting minerals. *Am. Mineral.* **85**, 543–556 (2000)
24. Archer, M.D., Nozik, A.J.: *Nanostructured and Photoelectrochemical Systems for Solar Photon Conversion*. World Scientific Publishing, Singapore (2008)
25. Cesar, I., Kay, A., Gonzalez Martinez, J.A., Grätzel, M.: Translucent thin film Fe_2O_3 photoanodes for efficient water splitting by sunlight: nanostructure-directing effect of Si-doping. *J. Am. Chem. Soc.* **128**, 4582–4583 (2006)
26. Mavroides, J.G., Kafalas, J.A., Kolesar, D.F.: Photoelectrolysis of water in cells with SrTiO_3 anodes. *Appl. Phys. Lett.* **28**, 241–243 (1976)
27. Fujishima, A.: Electrochemical photolysis of water at a semiconductor electrode. *Nature* **238**, 37–38 (1972)
28. Boddy, P.J.: Oxygen evolution on semiconducting TiO_2 . *J. Electrochem. Soc.* **115**, 199–203 (1968)
29. Grimes, C.A., Varghese, O.K., Ranjan, S.: *Light, Water, Hydrogen*. Springer Science & Business Media, Berlin (2007)
30. Sivula, K., Le Formal, F., Grätzel, M.: WO_3 – Fe_2O_3 photoanodes for water scaffold splitting: a host. Guest Absorber Approach *Chem. Mater.* **21**, 2862–2867 (2009)
31. Maeda, K., Domen, K.: Oxynitride materials for solar water splitting. *MRS Bull.* **36**, 25–31 (2011)
32. Nishijima, Y., Ueno, K., Yokota, Y., Murakoshi, K., Misawa, H.: Plasmon-assisted photocurrent generation from visible to near-infrared wavelength using a Au-nanorods/ TiO_2 electrode. *J. Phys. Chem. Lett.* **1**, 2031–2036 (2010)
33. Nishijima, Y., Nigorinuma, H., Rosa, L., Juodkazis, S.: Selective enhancement of infrared absorption with metal hole arrays. *Opt. Mater. Express* **2**, 1367–1377 (2012)
34. Tian, Y., Tatsuma, T.: Mechanisms and applications of plasmon-induced charge separation at TiO_2 films loaded with gold nanoparticles. *J. Am. Chem. Soc.* **127**, 7632–7637 (2005)
35. Sakai, N., Tatsuma, T.: Photovoltaic properties of glutathione-protected gold clusters adsorbed on TiO_2 electrodes. *Adv. Mater.* **22**, 3185–3188 (2010)
36. García, M.A.: Surface plasmons in metallic nanoparticles: fundamentals and applications. *J. Phys. D Appl. Phys.* **44**, 283001 (2011)
37. Centeno, A., Xie, F., Alford, N.: Light absorption and field enhancement in two-dimensional arrays of closely spaced silver nanoparticles. *J. Opt. Soc. Am. B* **28**, 325–330 (2011)
38. Catchpole, K.R., Polman, A.: Plasmonic solar cells. *Opt. Express* **16**, 21793–21800 (2008)
39. Beck, F.J., Verhagen, E., Mokkaapati, S., Polman, A., Catchpole, K.R.: Resonant SPP modes supported by discrete metal nanoparticles on high-index substrates. *Opt. Express* **19**, A146–A156 (2011)
40. Maier, S.A.: *Plasmonics: Fundamentals and Applications*. Springer, Berlin (2007)
41. Zhang, G., Wang, D.: Colloidal lithography-the art of nanochemical patterning. *Chem. Asian J.* **4**, 236–245 (2009)
42. Centeno, A., Breeze, J., Ahmed, B., Reehal, H., Alford, N.: Scattering of light into silicon by spherical and hemispherical silver nanoparticles. *Opt. Lett.* **35**, 76–78 (2009)
43. Liu, Z., Hou, W., Pavaskar, P., Aykol, M., Cronin, S.B.: Plasmon resonant enhancement of photocatalytic water splitting under visible illumination. *Nano Lett.* **11**, 1111–1116 (2010)
44. Naseri, N., Amiri, M., Moshfegh, A.Z.: Visible photoenhanced current–voltage characteristics of Au : TiO_2 nanocomposite thin films as photoanodes. *J. Phys. D Appl. Phys.* **43**, 105405 (2010)

45. Chandrasekharan, N., Kamat, P.V.: Improving the photoelectrochemical performance of nanostructured TiO_2 films by adsorption of gold nanoparticles. *J. Phys. Chem. B* **104**, 10851–10857 (2000)
46. Kittel, C.: *Introduction to Solid State Physics*. Wiley, NY (2004)
47. Petek, H., Ogawa, S.: Femtosecond time-resolved two-photon photoemission studies of electron dynamics in metals. *Prog. Surf. Sci.* **56**, 239–310 (1997)
48. Petek, H., Nagano, H., Ogawa, S.: Hole decoherence of d bands in copper. *Phys. Rev. Lett.* **83**, 832–835 (1999)
49. Sachtler, W., Dorgelo, G., Holscher, A.A.: The work function of gold. *Surf. Sci.* **5**, 221–229 (1966)
50. Giugni, A., et al.: Hot-electron nanoscopy using adiabatic compression of surface plasmons. *Nat. Nanotechnol.* **8**, 845–852 (2013)
51. Daniel, M.-C., Astruc, D.: Gold nanoparticles: assembly, supramolecular chemistry, quantum-size-related properties, and applications toward biology, catalysis, and nanotechnology. *Chem. Rev.* **104**, 293–346 (2004)
52. Knight, M.W., Sobhani, H., Nordlander, P., Halas, N.J.: Photodetection with active optical antennas. *Science* **332**, 702–704 (2011)
53. Mubeen, S., et al.: An autonomous photosynthetic device in which all charge carriers derive from surface plasmons. *Nat. Nanotechnol.* **8**, 247–251 (2013)
54. Mukherjee, S., et al.: Hot electrons do the impossible: plasmon-induced dissociation of H_2 on Au. *Nano Lett.* **13**, 240–247 (2013)
55. Cushing, S.K., et al.: Photocatalytic activity enhanced by plasmonic resonant energy transfer from metal to semiconductor. *J. Am. Chem. Soc.* **134**, 15033–15041 (2012)
56. Li, J., et al.: $\text{Ag@Cu}_2\text{O}$ core-shell nanoparticles as visible-light plasmonic photocatalysts. *ACS Catal.* **3**, 47–51 (2013)
57. Sundararaman, R., Narang, P., Jermyn, A.S., Goddard III, W.A., Atwater, H.A.: Theoretical predictions for hot-carrier generation from surface plasmon decay. *Nat. Commun.* **5**, 5788 (2014)
58. Manjavacas, A., Liu, J.G., Kulkarni, V., Nordlander, P.: Plasmon-induced hot carriers in metallic nanoparticles. *ACS Nano* **8**, 7630–7638 (2014)
59. Gorovov, A.O., Zhang, H., Gun'ko, Y.K.: Theory of photoinjection of hot plasmonic carriers from metal nanostructures into semiconductors and surface molecules. *J. Phys. Chem. C* **117**, 16616–16631 (2013)
60. Forbes, R.G., Deane, J.H.B.: Reformulation of the standard theory of Fowler-Nordheim tunnelling and cold field electron emission. *Proc. R. Soc. Lon. A. Math. Phys.* **463**, 2907–2927 (2007)
61. Murphy, E.L., Good Jr, R.H.: Thermionic emission, field emission, and the transition region. *Phys. Rev.* **102**, 1464 (1956)
62. Fowler, R.H. Nordheim, L.: Electron emission in intense electric fields. *Proc. R. Soc. Lond. A Math. Phys. Sci.* 173–181 (1928)
63. Lau, Y.Y., Liu, Y., Parker, R.K.: Electron emission: from the Fowler-Nordheim relation to the Child-Langmuir law. *Phys. Plasmas* **1**, 2082–2085 (1994)
64. Lin, H.Y., Chou, Y.Y., Cheng, C.L., Chen, Y.F.: Giant enhancement of band edge emission based on ZnO/TiO_2 nanocomposites. *Opt. Express* **15**, 13832–13837 (2007)
65. Hernández-Martínez, P. Govorov, A.: Exciton energy transfer between nanoparticles and nanowires. *Phys. Rev. B* **78**, (2008)
66. Neretina, S., et al.: Plasmon field effects on the nonradiative relaxation of hot electrons in an electronically quantized system: CdTe-Au core-shell nanowires. *Nano Lett.* **8**, 2410–2418 (2008)
67. Makhal, A., et al.: Dynamics of light harvesting in ZnO nanoparticles. *Nanotechnology* **21**, 265703 (2010)
68. Andrews, D.L.: A unified theory of radiative and radiationless molecular energy transfer. *Chem. Phys.* **135**, 195–201 (1989)

69. Andrews, D.L., Bradshaw, D.S.: Virtual photons, dipole fields and energy transfer: a quantum electrodynamical approach. *Eur. J. Phys.* **25**, 845–858 (2004)
70. Andrews, D.L., Curutchet, C., Scholes, G.D.: Resonance energy transfer: Beyond the limits. *Laser Photon. Rev.* **5**, 114–123 (2010)
71. Fox, M.: *Optical Properties of Solids*. Oxford University Press, Oxford (2010)
72. Furube, A., Du, L., Hara, K., Katoh, R., Tachiya, M.: Ultrafast plasmon-induced electron transfer from gold nanodots into TiO₂ nanoparticles. *J. Am. Chem. Soc.* **129**, 14852–14853 (2007)
73. Karp, G.: *Cell and Molecular Biology*. Wiley, NY (2009)
74. Allongue, P.: In: Bockris, J., Conway, B.E. White, R.E. (eds.) *Modern Aspects of Electrochemistry*. vol. 23, pp. 239–314 (1992)
75. Patel, M., Mallia, G., Liborio, L., Harrison, N.M.: Water adsorption on rutile TiO₂ (110) for applications in solar hydrogen production: a systematic hybrid-exchange density functional study. *Phys. Rev. B* **86**, 045302 (2012)
76. Blomquist, J., Walle, L.E., Uvdal, P., Borg, A., Sandell, A.: Water dissociation on single crystalline anatase TiO₂ (001) studied by photoelectron spectroscopy. *J. Phys. Chem. C* **112**, 16616–16621 (2008)
77. Sumita, M., Hu, C., Tateyama, Y.: Interface water on TiO₂ anatase (101) and (001) surfaces: first-principles study with TiO₂ slabs dipped in bulk water. *J. Phys. Chem. C* **114**, 18529–18537 (2010)
78. Walle, L.E., et al.: Mixed dissociative and molecular water adsorption on anatase TiO₂ (101). *J. Phys. Chem. C* **115**, 9545–9550 (2011)
79. Yang, H.G., et al.: Anatase TiO₂ single crystals with a large percentage of reactive facets. *Nature* **453**, 638–641 (2008)
80. Grinter, D.C., Nicotra, M., Thornton, G.: Acetic acid adsorption on anatase TiO₂ (101). *J. Phys. Chem. C* **116**, 11643–11651 (2012)
81. Silva, V.F., et al.: Substrate-controlled allotropic phases and growth orientation of TiO₂ epitaxial thin films. *J. Appl. Cryst.* **43**, 1502–1512 (2010). doi:[10.1107/S0021889810041221](https://doi.org/10.1107/S0021889810041221)
82. Hitosugi, T., et al.: Fabrication of TiO₂-based transparent conducting oxide films on glass by pulsed laser deposition. *Jpn. J. Appl. Phys.* **46**, L86–L88 (2007)
83. Hitosugi, T., et al.: Electronic band structure of transparent conductor: Nb-doped anatase TiO₂. *Appl. Phys. Express* **1**, 111203 (2008)
84. Hsieh, C., et al.: Monophasic TiO₂ films deposited on SrTiO₃ (100) by pulsed laser ablation. *J. Appl. Phys.* **92**, 2518–2523 (2002)
85. Nakamura, R., Okamura, T., Ohashi, N., Imanishi, A., Nakato, Y.: Molecular mechanisms of photoinduced oxygen evolution, PL emission, and surface roughening at atomically smooth (110) and (100) n-TiO₂ (Rutile) surfaces in aqueous acidic solutions. *J. Am. Chem. Soc.* **127**, 12975–12983 (2005)
86. Yamamoto, S., Sumita, T., Miyashita, A.: Preparation of TiO₂-anatase film on Si (001) substrate with TiN and SrTiO₃ as buffer layers. *J. Phys. Condens. Matter* **13**, 2875 (2001)
87. McDaniel, M.D., Posadas, A., Wang, T., Demkov, A.A., Ekerdt, J.G.: Growth and characterization of epitaxial anatase TiO₂ (001) on SrTiO₃-buffered Si (001) using atomic layer deposition. *Thin Solid Films* **520**, 6525–6530 (2012)
88. Sanches, F.F., Mallia, G., Liborio, L., Diebold, U., Harrison, N.M.: Hybrid exchange density functional study of vicinal anatase TiO₂ surfaces. *Phys. Rev. B* **89**(24), 5309 (2014)
89. Furubayashi, Y., et al.: A transparent metal: Nb-doped anatase TiO₂. *Appl. Phys. Lett.* **86**(25), 2101 (2005)
90. Furubayashi, Y., et al.: Novel transparent conducting oxide: anatase TiNbO. *Thin Solid Films* **496**, 157–159 (2006)
91. Hitosugi, T., et al.: Transparent conducting properties of anatase Ti_{0.94}Nb_{0.06}O₂ polycrystalline films on glass substrate. *Thin Solid Films* **516**, 5750–5753 (2008)

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