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Capturing Irradiation with Nano-antennae: Plasmon- induced Enhancement of Photoelectrolysis

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“It surprises me how disinterested we are today about things like physics, space, the universe and philosophy of our existence, our purpose, our final destination. It’s a crazy world out there. **Be curious.**”

— Stephen Hawking

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1 Introduction

Historically, the human civilization has exploited a variety of dominant energy resources over centuries during its early development. Up until far into the 18th century, mankind lived in the first solar civilization; exclusively renewable energies such as wind and water were utilized, finally by one billion people. The 19th century was that of coal, and for the first time, energy renewability was left for the benefit of energy exhaustibility. At the end of the 19th and then in the 20th century, mineral oil, natural gas, and nuclear fission emerged. Never was only one energy form in use, never did a new energy replace fully its predecessors; the increasing energy demand of a growing world population needed them all. The energy mix, however, was subject to constant change. With the advent of coal, the different forms of renewable energies of the first solar civilization were reduced to a remnant.

Energy should not be a luxury, but a commodity that everyone needs, in addition to food, water and shelter. What will then the 21st century stand for, when the energy requirements of now seven billion people, in the future nine or ten billion have to be met? Reasons for the energy crisis we are heading towards in the coming years are manifold, e.g. the growing demand for energy, highly overpopulated areas, such as China, India, Brazil and Nigeria, fossil fuel depletion, climate changes and the necessity to reduce carbon dioxide emissions. The UN has agreed to reduce carbon dioxide emissions by 25 – 40% by 2020; in addition to that, the European Union (EU) has made a commitment of a 20% reduction in greenhouse gases by 2020, and a 20% supply from renewables ¹. The forecasts of the European energy supply largely rely on fossil fuels, often with reduced security on the energy imports, and strong threats to the ecosystem. There is therefore a need to enlarge and diversify the energy supply using clean and renewable sources and to increase the efficiencies and cost

effectiveness of energy conversion technologies, with the EU particularly involved in finding viable solutions. Implementing these strategies with proper sustainable development has economic, ecological, and social benefits that insure the security of energy supply and environmental welfare. All the aforementioned factors plausibly hint at the 21st century as that of the second solar civilization, thus becoming the century of energy sustainability when more energy forms will be added to the mix. All sorts of modern technologies will utilize the principal eight renewable energies: solar irradiance, water power, wind, biomass, ambient heat and tidal, geothermal and ocean thermal energies. Among renewable energy resources, solar energy is the most promising one, with the ability to cover an entire year's energy consumption by just one hour of irradiation on a surface the size of Bavaria, if almost 100% of the incoming solar energy could be converted ². The sun provides a colossal power of 120,000 TW every year, of which we can practically harvest 600 TW, in comparison to humble ~3 TW for wind or ~5 TW for hydroelectric sources. It is worth noting that the current global annual consumption of ~17 TW is predicted to almost double by the year 2050 to an average value of ~30 TW, then almost triple to an average of ~50 TW by 2100: drastic needs which can still be covered by solar power ³.

Hydrogen plays a major role in this strategy as it can be the bridge to the future where renewable energies can play a prevalent role. Producing hydrogen from water using renewable energy, the most promising one out there, solar energy, will guarantee the best of both worlds: a reliable resource and a clean fuel. But why the focus on Hydrogen? Hydrogen is an ideal energy carrier, its raw material is just water, it can be converted to other forms of energy in multiple ways, and can be stored in gaseous, liquid or metal hydride form. Despite its low energy density and storage complications, it can be transported over large distances through tanks, ships, or even underwater pipelines. In energy terms, its transport is a factor of five cheaper than the costs of transporting electricity through high-voltage cables ⁴. More importantly, it is a clean, environmental friendly fuel that doesn't produce any greenhouse gases other than water vapor in any of its phases of production, transportation or storage. Production of hydrogen via water electrolysis is the step towards the future. It has been identified as one of the Holy Grails even back in 1995 aiming at artificial photosynthesis ⁵.

It has no carbon footprint like the conventional methods of producing hydrocarbons. Even when burned or used as a power source, the only waste product of hydrogen is water vapor, again carbon free. Hydrogen is still with 88% the most abundant element on the planet ⁶. We should be living in a “Hydrogen Economy”, a term that was coined by John Bockris in the 1970s at a talk at the General Motors Technical Laboratory ⁷, and that had been previously mentioned by geneticist J.B.S. Haldane. Water, being hydrogen’s most abundant source should replace fossil fuels as its primary source with the latter being however strongly bound to oxygen, and energy is required for water to undergo splitting. With having an abundant source of hydrogen, and a reliable, clean renewable energy source, water splitting is the only permanent solution. The electrolysis process can be conveniently achieved via mimicking nature’s photosynthesis by collecting and storing solar energy through water splitting: a desirable approach that can solve the challenge of solar irradiation’s inconsistency. The latter is a major drawback in photovoltaic applications, another green route depicted below (cf. Figure 1.1) alongside fuel cells that can readily convert hydrogen to electricity in the energy triangle of the future.

Figure 1.1 Projected energy triangle of the future ⁸

An indispensable tool for electrochemical water splitting is the photoelectrochemical (PEC) cell, housing a semiconducting electrode, which is the key to incident light absorption. The semiconducting electrode or photoelectrode, being the photoanode in the scope of this work, is the main focus of any PEC system. The material has to be abundant, stable, easy to handle, relatively cheap, and with suitable band structure.

TiO₂ has been of great interest since the early 1970s after the demonstration of photocatalytic water splitting under ultraviolet irradiation in the pioneering work of Fujishima and Honda ⁹. Since then, a great deal of effort and research has been devoted to optimizing the performance of this oxide material and to circumvent its shortcomings. The large band gap of about 3 eV ¹⁰ hinders the light absorption in the visible region, automatically decreasing its overall efficiency. Photoconversion efficiencies of polycrystalline TiO₂ have not yet exceeded a value that will make it compatible with photovoltaic systems, coupled with electrolyzers, that have nowadays achieved impressive efficiency yields of ~ 33% ¹¹. Unfortunately, due to the intermittent nature of sunlight, a non-electrical storage system should accompany the process of solar harvesting, to avoid loss of unwanted or excess energy, bringing us back to chemical fuels as an attractive storage alternative.

Many routes have been followed to increase efficiencies with band gap engineering in its many forms, such as semiconductor doping, that will significantly decrease the band gap of TiO₂, shifting its absorption spectrum to the visible range. An example is the enhanced performance of carbon-doped TiO₂ nanotubes where band gaps have been efficiently reduced to 2.32 eV ¹². Studies have shown that photocurrents increase if the wall thickness of the tubes is reduced to a value less than the minority carrier diffusion length. Increase in the photocurrent was proven strongly influenced by the nanotube lengths ¹³ as well as by the overall tubular structure of vertically-oriented nanotube array geometry, which is advantageous in its large internal surface area and enhanced electron flow for vectorial charge transfer ¹⁴. Furthermore, introducing metal ions into the crystal lattice can cause what is referred to as “false valence band” (FVB) formation. The transition metal orbitals overlap to form a new band closer to the water oxidation potential. A new set of orbitals will be produced, at more negative

energy than the original. Control over the dopant is basically controlling the energy of the valence band. The new band gap, between the false valence band and the original conduction band, is smaller than the original band gap, enhancing the absorption of light in the visible region. Metal ion implantation is referred to as “2nd generation photocatalyst”¹⁵. Noble metal loading such as Gold or Silver, Platinum or Palladium, enhances the photo-induced reaction by supporting the electron transfer at the interface, and hindering charge recombination processes in the bulk. This increases the quantum yield, and shifts the onset of the photocurrent to lower photon energies.

In the present work, we will study much more promising photoanode systems such as the Au-doped TiO₂ nano-antennae and the Ag-doped BiVO₄ films that elegantly highlight the role of plasmonic enhancement. In Chapter 2, the history of photoelectrochemistry will be briefly discussed. The theory will be a guide to the general semiconductor properties, the solid-liquid interface and its characterization. The thermodynamics and the process of water splitting will be thoroughly explained, as well as the reason behind doping applications and their effect on PEC efficiencies and charge transfer facilitation. This will lead us to Chapter 3, where Raman Spectroscopy will be introduced alongside Surface Enhanced Raman Spectroscopy (SERS), the reasons behind the enhancement, and the arising plasmon modes which yield strong enhanced electric fields at the surface. Chapter 4 will describe in detail the photoanode fabrication as well as the basic mechanism of all measuring apparatuses and techniques used to further portray the photoanode, both electrochemically and spectroscopically. Chapter 5 will summarize all the results that characterize the semiconductor on a plasmonically active co-catalyst, a patterned structure which has not been investigated before: TiO₂ pillars on a Raman active Au substrate. Furthermore, the growth process parameters of BiVO₄ films deposited on Fluorine doped Tin Oxide (FTO) and their modification with Ag nanoparticles (AgNP) are briefly studied with a focus on the latter’s plasmonic resonance effects. In Chapter 6, all results will be interpreted and a general outlook is given about further PEC applications in view of the concept of artificial photosynthesis for a green future.

2 Photoelectrochemistry Fundamentals

2.1 History of Photoelectrochemistry

At the present times, there are several ways through which light can be converted into other energy forms. Apart from solar thermal power, the first is Nature's way of solar energy conversion: Photosynthesis, the conversion of CO_2 and H_2O to sugars, oxygen and biomass. It is the production of chemical fuels that are the reason for life as we know it, and its sustainability. The second is based on photovoltaic cells, using semiconducting absorbing surfaces to convert solar illumination to electrical energy. A technology present since almost 70 years, consisting of two solids connected via a microscopic junction that provides the cell with the ability to guide a unidirectional current flow and produce electric power. The third, and the focus of this thesis, is based on photoelectrochemical (PEC) cells. The latter could be considered a hybrid of the first two ways producing electricity or chemical fuels, or both, via a semiconducting electrode which is the key to incident light absorption. It is at the interface between semiconductor and liquid through which the chemical steps leading to energy conversion and photoelectrolysis take place.

Photoelectrolysis and the study of photoeffects are almost 200 years old ¹⁶. The field can be traced back to the first PEC experiment carried out by Becquerel, father of the photoelectric effect, back in 1839. Becquerel demonstrated that voltage and current were produced when he illuminated a Silver Chloride electrode immersed along with a counter electrode into an electrolytic solution. The latter photovoltaic phenomenon, called the "Becquerel Effect" was not well understood in the beginning, until it was later clarified by the work of Brattain and Garrett in 1954 ¹⁷, when they shed light on the properties associated with surface states at the semiconducting surfaces. The Becquerel effect was associated with

the semiconductor at the solid-electrolyte interface, or more specifically to the formation of the so-called semiconductor-electrolyte junction at the interface ¹⁸. It was then that the modern era of photoelectrochemistry was born. Brattain and Garrett explained how chemical reactions at the surface of germanium electrodes, followed by CdS, ZnS, CdSe, ZnSe, Si, ZnO and SrTiO₃, could be affected by altering the semiconductor properties, as well as by illumination. The quick development was fuelled by the discovery that when the impurities of semiconducting metals are controlled, their electrical and optical properties can be relatively easily manipulated.

Starting 1970 and up to 1972, a practical PEC system for solar energy conversion and storage was studied by Fujishima and Honda. The follow up work however, did not appear until 1975. The two pioneers illuminated a rutile TiO₂ anode with a black Platinum counter electrode ⁹, and showed that the oxidation of water could be achieved at potentials more negative than that of the standard redox potential of the H₂O/O₂ redox couple. They called it the “photosensitized electrolytic oxidation” ¹⁸ and suggested the use of the latter phenomenon for water splitting using sunlight.

2.2 Semiconductor Physics

A PEC cell is a device that can convert light energy into a different energy form, electrical or chemical, through light-induced electrochemical processes using a photoanode as its working electrode, alongside a corrosion resistant counter electrode, and a reference electrode, all immersed in one electrolyte. Metals with overlapping, partially filled bands are very unsuitable candidates for photoanodes, whereas semiconductors, with no overlapping bands, such as TiO₂ in this work, fulfill the photoanode requirements where light can excite electrons to achieve conductivity. Before carrying on any further, it is necessary to explain a few key terms that are needed to fully understand a PEC system: starting with metals and semiconductors, semiconductor-electrolyte junctions and the actual water splitting mechanism.

Metals exhibit high electrical conductivity and have a large number of free electrons moving in the lattice. The mobility of the electrons is due to the very strong interactions between neighboring atoms in the lattice. Orbitals of these sites overlap and form a continuum of energy levels, which is termed an energy band. Classically, all electrons would occupy the lowest energy levels giving rise to a Boltzmann distribution. However, the occupancy is constrained by the fermion nature of electrons as reflected in the Pauli Exclusion Principle, where each orbital can accommodate only two electrons with opposite spins, and thus much higher energy levels are occupied. The topmost occupied energy level at 0 K is the Fermi level, and the electron's Fermi-Dirac distribution function¹⁹ below is the probability of having an electron in a particular state with energy ε ,

$$f_e(\varepsilon) = \frac{1}{e^{\frac{(\varepsilon - \mu)}{k_B T}} + 1}$$

with μ being the chemical potential of electrons, T the absolute temperature, and k_B Boltzmann's constant. The distribution function for holes is $f_h(\varepsilon) = 1 - f_e(\varepsilon)$.

In the presence of an electric field, provided the band is partially occupied, electrons are excited into levels with a motion directed along that field, causing a subsequent current flow. At finite temperatures, partial occupancy of the electron distribution will lead to electronic conductivity. Poor overlapping in transition metal oxides causes insufficient energy in the band to overcome electron repulsion effects as the electrons migrate, resulting in electron localization on specific lattice sites making the aforementioned oxides act as semiconductors.

The most important difference between metals and semiconductors lies in the band occupancy. Unlike metals, the semiconductor bands are at least at 0 K completely occupied or empty, leading to low conductivity. The Highest Occupied Molecular Orbital is called the HOMO, and the Lowest Unoccupied Molecular Orbital is called the LUMO. The highest bonding molecular orbital and the lowest anti-bonding molecular orbital are separated by the HOMO-LUMO gap. Bonding and anti-bonding orbitals tend to cluster together into tightly packed groups, forming "continuous" bands of energy levels and thus one band is considered a

single block of energy. The cluster of fully occupied bonding orbitals is referred to as the Valence Band (VB), and the cluster of vacant anti-bonding orbitals as the Conduction Band (CB). According to latter notations, the HOMO-LUMO gap is called the band gap E_g (*cf.* Figure 2.1). Associated with each of the CB and VB is the bandwidth, the energy difference between the orbitals of highest and lowest energy in the band.

Figure 2.1 Schematic representation of a semiconductor energy band structure (left), theoretical representation of the energy band structure for TiO_2 (right)²⁰

Shaded areas denote fully occupied bands and unshaded areas vacant bands in the figure on the left. Two non-valence bands are depicted to stress the fact that the VB is the highest occupied band. When photons with energy greater than the band gap are absorbed by the semiconductor, electrons are excited from the VB to the CB. If the band gap is small *i.e.* < 1.0 eV, then intrinsic thermal excitation of an electron from the VB to the CB can take place, even at room temperature ($k_B T = 26$ meV). In an ionic crystal, such as TiO_2 , the VB is composed of orbitals derived from filled $2p$ orbitals of O^{2-} , and the CB from empty $3d$ orbitals of Ti^{4+} .

The chemical reactivity of a semiconductor is related to the value of the band gap. As for their use in photoelectrochemistry, a large band gap semiconductor only absorbs at short wavelengths and will not absorb from sunlight as many

photons as small band gap semiconductors do, making the band gap a limiting factor in PEC efficiencies as it limits solar harvesting and conversion. One would assume that the smaller the band gap, the higher the absorption efficiency. When one however contemplates the spectral distribution of sunlight under Air Mass (AM) 1.5 conditions (referring to a standard measurement condition when the Sun is at a zenith angle of 48.2° above the horizon), it is clear why the first assumption is not quite true. To harvest the maximum of the solar spectrum, semiconductors of band gap ranging between 2.0 - 2.8 eV seem quite promising as they absorb in the range with highest irradiance (*cf.* Figure 2.2).

Figure 2.2 Spectral distribution of sunlight under AM 1.5 conditions ¹⁵

For $h\nu = E_g$, photon absorption leads to an optical transition that produces an electron in the conduction band, where the excited electron is available for an electrochemical reaction. In the case of $h\nu > E_g$, photon absorption leads to excited states with energies larger than that of the conduction band edge, resulting in the dissipation of significant amounts of energy as heat, which decreases the overall efficiency.

Direct band gap semiconductors are those that have a fully allowed transition between VB and CB, so light is strongly absorbed close to the solid surface. The minimum of the CB lies just above the VB maximum, so single photon absorption is therefore sufficient for the transition (*cf.* Figure 2.3). As for indirect band gap

semiconductors, the lowest energy electronic transition between VB and CB is formally optically forbidden, and therefore a two-step process is required, which includes a change in both energy and momentum, each with alternatively a single phonon absorption.

Figure 2.3 Schematic view of allowed direct and indirect optical transitions

The absorption coefficient (α) for the aforementioned allowed transitions is best described below with A' being a proportionality constant^{21,22}.

$$\alpha_{direct} = A'(h\nu - E_g)^{0.5}$$

$$\alpha_{indirect} = A'(h\nu - E_g)^2$$

The fact that indirect transitions requiring two steps are less probable, leads to larger useable range of wavelengths and higher absorption coefficients due to larger penetration depths, such as for Si ($E_g = 1.2$ eV), which is an indirect band gap. In contrast to direct band gap semiconductors like GaAs ($E_g = 1.42$ eV), (cf. Figure 2.4), a drastic drop is observed after a sharp onset of absorption threshold is reached at band gap energy.

For PEC purposes, samples must not be resistive, because energy will then be lost as charge carriers travel through the semiconductor. To control this unwanted resistivity and the losses associated with it, resistance is decreased in a doping process. Doping consists of introducing impurity atoms into the crystal, and dopants are classified into either electron donors or acceptors. Donors produce a positive charge on the dopant atom (cf. Figure 2.5) and an electron in the CB, leaving a hole in the VB.

Figure 2.4 Plot for the absorption coefficient vs. photon wavelength for Si and GaAs ¹⁵

This material which is donor-doped is referred to as *n*-type since this procedure creates free electrons, the majority carriers, possessing a *negative* charge and hence the naming. Similarly, acceptors produce a negative charge on the dopant atom and a hole in the VB, the *positive* majority carriers make this material *p*-type.

Figure 2.5 Basic bond pictures of a semiconductor (a) Intrinsic Si with no impurities (b) *n*-type Si with donor impurities (Phosphorous) (c) *p*-type Si with acceptor impurities (Boron) ²³

An important quantity mentioned earlier is the Fermi level E_F of the solid, determining the tendency of a semiconductor to transfer charges to other phases in direct contact. The Nernst equation below describes the electrode potential of the electrolyte phase for solutions that contain acceptors (A) and donors (D),

$$E\left(\frac{A}{D}\right) = E^0\left(\frac{A}{D}\right) + \frac{kT}{n_e} \ln \frac{[A]}{[D]}$$

where $E\left(\frac{A}{D}\right)$ is the actual electrochemical potential of the solution, $E^0\left(\frac{A}{D}\right)$ is the formal electrode potential of the redox couple, n_e is number of electrons per mole of the redox couple, $[A]$ and $[D]$ are the respective concentrations of acceptor and donor species which represent oxidizing and reducing agents respectively.

Figure 2.6 Energy band diagram, density of states $N(E)$, Fermi-Dirac distribution functions $f_e(\epsilon)$ and charge carrier density for (a) intrinsic (b) n-type (c) p-type semiconductors in thermal equilibrium – based on ²³

At 0 K, the Fermi level of an intrinsic semiconductor would be located approximately in the middle of the bandgap (*cf.* Figure 2.6 (a)). The states in the VB would be fully occupied, and the probability of finding an electron there is 1. The states in the CB would be fully vacant and the probability of finding an electron there is 0. The probability of finding an electron at the Fermi level is 0.5, in contrast to the definition of the Fermi level in metallic solids. For doped semiconductors, the Fermi level will shift, since doping will influence the tendency to lose or gain electrons. For *n*-type semiconductors (*cf.* Figure 2.6 (b)), the Fermi level is located just below the CB, it may actually collapse into the CB for very heavy doping, making it a degenerate semiconductor, which then acts more like a metal. Similarly for *p*-type semiconductors (*cf.* Figure 2.6 (c)), where the Fermi level lies between the acceptor level and the top of the valence band ⁴. Upon illumination, the generated charge carriers cause a free energy shift and therefore a perturbation of the equilibrium in the semiconductor. The relaxation to the equilibrium state occurs either by utilizing the majority carriers in surface reactions, or via electron-hole recombination processes. Excess energy can be emitted radiatively (fluorescence) in the form of a photon, or just dissipated non-radiatively as heat. However, the targeted overall equilibrium is not always achieved, but with each of the CB and VB having an individual population that is internally in equilibrium (*cf.* Figure 2.7). The fact that the bands are then not in equilibrium with respect to electron exchange introduces the concept of separate *quasi*-Fermi levels E_F^* (sometimes referred to as *imref*) for each band, as it is not possible to describe the carrier populations by a single Fermi level.

Figure 2.7 Fermi level in an *n*-type semiconductor in the dark (a) and its splitting into $E_{F,n}^*$ and $E_{F,p}^*$ under illumination with lower (b) and higher light intensity (c) – based on ²⁴

2.3 Semiconductor-Electrolyte Interface

To discuss water splitting at a photoanode, it is necessary to explain the consequences of bringing a semiconductor in contact with an aqueous electrolyte. Consider an *n*-type semiconductor immersed in an electrolyte, exchange of charge carriers occurs in both the semiconductor and the semiconductor-electrolyte interface until equilibrium is established. Like charging a capacitor, the process continues until the initial difference in the electrochemical potentials is neutralized and no further charge transfer is thermodynamically possible. Once that happens, the equilibrium potential of the electrons in the semiconductor and that of the solution will be the same, and consequently their respective Fermi levels. The key factor allowing semiconductor-electrolyte junctions to separate charge effectively is the electric field present at the interface which can reach the order of 10^5 V/cm¹⁵. The latter process leads to band bending and the formation of a space charge layer (SCL), which is compensated by a localized Helmholtz layer in the electrolyte. A diffusion layer is formed between the SCL and the bulk semiconductor where charge carriers recombine. The SCL could either be a depletion layer (DL) or an accumulation layer (AL) depending on the Fermi levels of each of the semiconductor $E_{F,SC}$ and that of the redox couple in the electrolyte $E_{F,OR}$.

Figure 2.8 Differential capacity of the space charge layer and Mott-Schottky plot of an *n*-type semiconductor²⁵

Band bending, which can be described as a barrier stretching from the bulk to the interface, doesn't occur when the excess charge in the SCL of the semiconductor is zero, a case in which one speaks of a flat band potential U_{FB} . This concept is paralleled the point of zero charge (pzc) in a metal-electrolyte interface. The energy of the electrons at band edges from the bulk and up to the surface is constant. It can be accurately determined using electrolyte electroreflectance (EER), which takes into account recombination kinetics, hole trapping at surface defects as well as hole accumulation due to poor charge transform kinetics ²⁶. The more common method however is to form the intercept of the Mott-Schottky plot (*cf.* Figure 2.8) for capacity measurements by extrapolating the value of the inverse square capacitance to zero. It is clear from Figure 2.8 that for $U < U_{FB}$, an AL is formed due to accumulating electrons on the surface, which can reach up to a width of 100 Å. For $U > U_{FB}$, a DL is formed, reaching up to micrometers into the electrolyte ¹⁵, where positive charges are depleted, causing negative counter ions to compensate for the charge at the interface. The dark grey markers initiating at the CB (*cf.* Figure 2.9) represent the potential drop of value $-e_0\Delta\phi_{SC}$, showing clearly a wider depletion layer. For $U \gg U_{FB}$, a deep DL is formed and eventually an inversion layer at $U \gg \gg U_{FB}$ ensues, where now holes are the dominant species.

Figure 2.9 Band bending at an n -type semiconductor-electrolyte interface (a) U_{FB} conveying no excess charge (b) Accumulation layer (c) Depletion layer formation – based on ⁷

Charge separation abilities in the AL are minimal relative to that of the DL, and the electric field gradient is reduced. Only charge carriers very close to the interface will sense the excess charges and be separated by the field. This is the reason why the semiconductor-electrolyte interface in accumulation is not useful for solar energy harvesting and conversion, as the electric field is reversed and holes are then not transported.

2.4 Water Splitting Thermodynamics

After discussing the semiconductor-electrolyte interface, it is now vital to introduce a new factor that will drive the water splitting reaction: illumination. Thermodynamically, at standard pressure and temperature, the Gibbs free energy ΔG for the water splitting is positive, and hence it is not a spontaneous reaction. The conversion from electrical to chemical energy takes place at the semiconductor-electrolyte interface through charge transfer.

A potential difference U , applied between anode and cathode does a work nFU , where F is the Faraday constant, and n the number of moles of electrons involved in the reaction. Let $U_{\min}$ be the minimum voltage needed to drive the water splitting reaction then $\Delta G = nFU_{\min}$, this is the maximum work that can be derived from the system by the reverse reaction. At 25°C and 1 bar, ΔG for water splitting is 237.178 kJ/mol, setting $U_{\min}$ at 1.229 V⁸. This requires a minimum E_g of ~1.23 eV, with the CB ideally slightly above the water reduction potential, *i.e.* at a value more negative than U_{H^+/H_2} (electrochemical scale) and the VB slightly below the water oxidation potential, *i.e.* at a value more positive than U_{H_2O/O_2} .

The focus of this work is on widespread oxide semiconductors which are relatively cheaper, stable and photocorrosion resistant, but unfortunately of large band gap, absorbing in the ultraviolet (UV) range in normal circumstances. Under operating conditions, the conduction band edge must be more negative than the standard redox potential for proton reduction on the electrochemical scale, and

the valence band edge more positive than the oxidation potential of water in the oxygen evolution reaction.

An overview of several oxide materials (*cf.* Figure 2.10) highlights the different band edges with respect to redox potential energies versus the normal hydrogen electrode (NHE) and the vacuum level (+4.44 eV above NHE) ^{8,27}. The negative notation on the vacuum level is based on the work function principle ²⁸, the energy required to remove an electron from a particular state in the solid into the vacuum when the electrode is at 0 V vs. NHE. Hence, the more tightly bound electrons have higher positive energies.

Figure 2.10 Band gap energy of different oxide materials, showing their relative positions to water redox potentials, with respect to vacuum level (left ordinate) and NHE (right ordinate) in an electrolyte of pH = 2 ²⁹

The charge balance across the interface is potential dependent, which makes the Helmholtz layer dependent on $[H^+]$ or $[OH^-]$ changes in the electrolyte. This pH change subsequently influences the U_{FB} and causes a shift in the semiconductor's band edges (*cf.* Figure 2.11), following the Nernst slope at 59 mV per pH-unit from the equation $E = E_0 - \frac{2.3 RT}{nF} \log[H^+]$.

Figure 2.11 Electrolyte pH effect on TiO_2 band edges with respect to vacuum level and NHE ²⁹

Consider irradiating an *n*-type semiconductor illuminated with a suitable energy ($h\nu \geq E_g$), incoming photons are absorbed and the main reactions ideally taking place are:

- $2h\nu + \text{semiconductor} \rightarrow 2h^+ + 2e^-$ (electron-hole generation)
- Simultaneous charge separation and migration of majority charge carriers (electrons) through the photoanode to the backside electrical contact, and minority carriers (holes) to the photoanode-electrolyte interface. This charge separation is accomplished by the help of the electric field present in the depletion layer.
- $\text{H}_2\text{O} + 2h^+ \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+$ (oxidation at the photoanode)
- Transport of H^+ ions through the electrolyte, and of electrons via the external circuit from photoanode to cathode.
- $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ (reduction at the cathode)

The photovoltage between the electrodes driving charges through the circuit and supplying carriers for O_2 and H_2 generation is nothing other than the net gain in

free energy, which at zero current is called the open circuit potential (OCP). Under dark conditions, the Fermi levels of the electrodes equalize with the electrolyte redox potential³⁰ and both CB and VB are bent with the upper threshold of the barrier height being the OCP. For that reason the latter can never exceed the required voltage of ~1.23 V for water splitting, causing this process to be an assisted one, in need of a bias, and more suitable for semiconductors with band gaps larger than 1.23 eV. The external bias, also dependent on pH, provides sustainable current flow and increases band bending to maintain the charge separation driven by the electric field.

2.5 Photometric Efficiencies

The bias to be applied is equal to the potential difference between that of the photoelectrode potential and the OCP, making the solar-to-hydrogen (STH) efficiency naturally dependent on the bias voltage:

$$\eta_{STH} = \frac{P_{out} - P_{in}}{P_{light}} = \frac{J_{photo}(U_{redox} - U_{bias})}{P_{light}}$$

where $U_{redox} = U_{min} \cong 1.23$ V, and J_{photo} the photocurrent density generated upon irradiating with a beam of power density P_{light} . A more useful parameter for the evaluation of performance is the incident photon-to-current conversion efficiency (IPCE), also called the external quantum efficiency. It measures the effectiveness in converting photons incident on the illuminated area to the photocurrent flowing between the electrodes.

$$IPCE(\lambda) = \left(\frac{hc}{e}\right) \left(\frac{J_{photo}(\lambda)}{P_{light}(\lambda)\lambda}\right) = 1240 \left(\frac{J_{photo}(\lambda)}{P_{light}(\lambda)\lambda}\right)$$

The IPCE takes a value of 100% when all photons generate electron-hole pairs, but this is mostly less than 100% due to reflection losses, absorption by the electrolyte, or lack thereof, by the semiconductor, as well as recombination of charge carriers.

Another parameter that can be measured to value the performance of a PEC system is the absorbed photon-to-current conversion efficiency (APCE), also called the internal quantum efficiency, and related to IPCE *via*:

$$APCE(\lambda) = \frac{IPCE(\lambda)}{1 - 10^{-A}} = \frac{IPCE(\lambda)}{A(\lambda)} = \frac{IPCE(\lambda)}{1 - R - T}$$

where R , T and A are the optical reflection, transmission and absorption respectively (not to be confused with the absorption coefficient α). The APCE corrects for reflection and scattering losses, and is herewith more accurate when evaluating recombination losses in the SCL which was addressed by Wilson ³¹, Reichman ³² and Jarrett ³³ as an improvement to the original photocurrent response evaluation of a system described by Gärtner ³⁴ as :

$$I_{photo} = qP_{light} \left[1 - \frac{e^{-\alpha W}}{1 + \alpha L_p} \right]$$

where q is the elementary charge, W is the width of the SCL and L_p the diffusion length of the minority carriers in the semiconductor. The IPCE remains however the most widespread method for determining device-level efficiency. As it is measured under monochromatic irradiation, it could be used to predict photocurrent generation under actual solar irradiation:

$$J_{solar} = \int (IPCE(\lambda) \times \Phi(\lambda) \times e) d\lambda$$

where J_{solar} is total solar photocurrent density and $\Phi(\lambda)$ is the solar photon flux in photons/m²/s.

2.6 Light Trapping

On another note, the water splitting mechanism and photocurrent generation described in Section 2.5 not only applies in the ideal case, i.e. where reflection losses are minimal, or recombination of charge carriers are hindered, but also to an ideal compact photoanode consisting of a defect-free thin film. The photoanode studied in this work is a complex nanostructured oxide semiconductor anchored on a noble metal, making the photocurrent dependent on the photogenerated charge carrier efficiency and not only on the potential gradient over the SCL which, in the case of an *n*-type semiconductor, is the DL. Charge transfer takes place via an iso-energetic process of tunneling, requiring that the fluctuating energy level of the electrolyte species be instantaneously equal to that of electrons or holes in the semiconductor. In a polar solvent like H₂O, solvent ions tend to rearrange themselves after a redox reaction takes place, in order to accommodate for loss or gain of charge. During electron transfer, the ion energy level remains the same, according to the Frank-Condon principle, making the electron transfer, whose rate is proportional to the majority carrier concentration in the semiconductor and the density of states of the electrolyte species, faster than the ion reorganization. It is rather clear at this stage how important the charge transfer mechanism is on the photocurrent generation and subsequently the PEC efficiency of a system upon its interaction with incident light. The charge separation and consequent charge transfer would not occur if it would not be for the electric field at the interface.

Another phenomenon that probes the interaction of a system's building blocks with incident light, as well as electric field effects and enhancements is Raman spectroscopy. The latter will be discussed in detail in Chapter 3, but it is crucial to point out that it is due to the aim at hybridizing the aforementioned phenomena, that the photoanode was designed as described. The nanostructured surface enhances both the Raman effect of the incoming light, due to optical and electronic properties of a microstructured but ordered morphology, as well as enhancing the photoresponse of TiO₂ in the visible region due to the Au metal

substrate. Metals are covered with electrons arising from conduction electrons of the lattice due to the presence of positive charges in their center. When the free metal electrons interact with light, they oscillate collectively at the surface, with these oscillations being defined as plasmons having a resonance frequency at which they absorb or scatter light most efficiently, depending on the metal nature and surface shape. Plasmonic nanostructures have two main pathways for increasing the solar conversion efficiency which will form the backbone of this work. The first, more obvious way, is by enhancing the semiconductor's ability to absorb light through increasing the optical path length and concentrating the incident field. The second pathway is by transferring the metal plasmon energy to the semiconductor directly via plasmon-induced resonance energy transfer (PIRET) which would induce the charge separation. When HOMO and LUMO levels align symmetrically about the metal Fermi level, light with half the gap energy can be enough to make the transition. The metal then acts as a charge transfer intermediate, where a spectroscopic transition that usually takes place in the UV can ultimately be excited by visible light ³⁵.

3 Raman Spectroscopy

3.1 From Rayleigh to Stokes Scattering

Why is the sky blue? Why is the sunset red? Such simple questions with not so trivial answers are behind the revelation of Raman Spectroscopy. Back in 1859, physicist John Tyndall placed the first stepping stone in a long array of discoveries regarding light's interaction with matter using his air purification experiments. When shining intense light through it, the latter would scatter off dust particles as blue tinted, and light of a longer wavelength, that would pass through would be relatively red tinted. Tyndall extrapolated this knowledge to the color of the sky when, combining with what physicists knew at the time about the white light spectrum and color separation using a prism, he was able to explain how sunlight scattered off air pockets makes the sky appear blue, and unscattered light makes us perceive the sun as red. In 1904, Lord Rayleigh examined the Tyndall effect more closely, in light of Maxwell's electromagnetic theory. Based on Maxwell's electrodynamic theory, the classical theory of light scattering on small particles has been proposed by Rayleigh. This describes the elastic scattering of light on small particles, with the same wavelength for the incident and scattered light. As for molecules, the outcome is somewhat different. In 1923, Adolf Smekal predicted that light scattered off a molecule is reemitted at a different energy of the incident radiation in a molecular-vibronic effect. This effect was later verified experimentally by Sir Chandrasekhara Venkata Raman in 1928, winning him the Nobel Prize in 1930 and naming the phenomenon in his honor.

If a normal mode in the molecule then vibrates with a frequency ν , then the electromagnetic oscillation can be expressed as :

$$E = E_0 \cos 2\pi\nu_0 t$$

An incoming EM wave causes a periodical deformation of the electron cloud inducing an oscillatory dipole μ ³⁶. The induced dipole is related to the incident field E of incident frequency ν_0 by the polarizability α with $\mu = \alpha E$. Since the polarizability depends strongly on the type of bonds within the molecule, Raman scattering can be used as an analytical technique to sensitively determine the molecular structure and chemical identity of a compound in a given environment.

With the ever increasing catalog of chemicals and reactions, Raman Spectroscopy can act as a quick and non-destructive method to identify fingerprint spectra as many organic molecules are composed of basically the same elements of hydrogen, carbon and oxygen. Infrared (IR) Spectroscopy is a similar technique to Raman Spectroscopy, both offering access to the vibrations of the molecular skeletons, with high intensity lasers in the visible (VIS) or near-infrared (NIR). IR absorption is a *one-photon* process, where the molecular property involved in the resonant interaction is the change in the *dipole moment* as a result of molecular vibrational motion. Raman scattering in contrast, is a *two-photon* process, where the molecular property involved is the *molecular polarizability* which is modulated by vibrational motion³⁷. Light scattered by this modulated induced dipole consists of both Rayleigh and Raman scattered components, where for the former the light scatters at the incident frequency ν_0 , while in the latter a frequency shift is observed. This frequency shift is due to the excitation of vibrations, by which energy is lost or gained in the molecule. The vibrational states of the molecule are best approximated in a Morse-type potential, where the spacing between energetic levels decreases as the dissociation limit is approached. Since that remains far below the dissociation limit, a discussion based on the harmonic oscillator model, with evenly spaced energy levels of $\hbar\omega = h\nu$, is sufficient. A further simplification is the discussion within classical theory.

The wavenumber of the line emitted (or absorbed) by a harmonic oscillator of intermolecular bond strength force constant K and reduced mass μ is ³⁶:

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

experimentally explaining why the lighter the molecules, the higher the frequency. The fact that the frequency of the emitted line is influenced by the reduced mass μ is exploited in the isotopic effect when parts of a molecule are substituted by chemically equivalent components of different mass (e.g. H with Deuterium) helping to disentangle the IR band structure.

The nuclear displacement Q of the normal coordinate will then be given by:

$$Q(t) = Q_0 \cos 2\pi\nu t = Q_0 \cos \omega t$$

where Q_0 is the vibrational amplitude. Since the latter is small enough, the polarizability α can be then described as a linear function of Q :

$$\alpha = \alpha_0 + \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q(t)$$

where α_0 is the polarizability in the equilibrium configuration and $\left(\frac{\partial\alpha}{\partial Q}\right)_0$ the rate of change of polarizability with respect to the nuclear coordinate change Q . The oscillating normal coordinate $Q(t)$ brings about a modulation of the molecular polarizability α with the frequency ν of the normal mode. Combining all the equations above will lead to:

$$\begin{aligned} \mu(t) &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q_0 E_0 \cos 2\pi\nu_0 t \cdot \cos 2\pi\nu t \\ &= \alpha_0 E_0 \cos 2\pi\nu_0 t + \frac{1}{2} \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q_0 E_0 [\cos\{2\pi(\nu_0 - \nu)t\} + \cos\{2\pi(\nu_0 + \nu)t\}] \end{aligned}$$

As mentioned before in the case of Rayleigh scattering, a molecule that undergoes excitation to a virtual state and returns to its original vibrational state during relaxation, will scatter at its incident frequency ν_0 , which is the first term of the equation above (*cf.* Figure 3.1 (a)). As for Raman scattering, the molecule can transit to a higher vibrational state emitting a photon of frequency $(\nu_0 - \nu)$, in the so-called Stokes scattering, described in the second term of the equation above (*cf.* Figure 3.1 (b)). Alternatively, the molecule can transit from a higher stationary state to a lower stationary state by emitting a photon of frequency $(\nu_0 + \nu)$, in the so-called anti-Stokes scattering, described in the third term of the above equation (*cf.* Figure 3.1 (c)). Dotted lines represent the virtual state, with S and n being respective electronic and vibrational states. Needless to say, the term $\left(\frac{\partial \alpha}{\partial Q}\right)$ is the most significant as it denotes the change of polarizability, without which the Raman scattering term will converge to zero.

Figure 3.1 Schematic band energy representation showing different transitions in Rayleigh and Raman (Stokes and anti-Stokes) Scattering. The dotted line represents the so-called virtual state of the molecule, where no definite energy value can be assigned.

3.2 Surface Enhanced Raman Spectroscopy (SERS)

The intensity (I) of Raman Scattering is given by:

$$I = Cl \left(\frac{\partial \alpha}{\partial Q} \right)^2 \omega^4$$

Where C is a collection of constants including the speed of light, l is the laser power, ω is the frequency of the scattered light, and $\frac{\partial \alpha}{\partial Q}$ the change of molecular polarizability³⁶. The intensity of Raman scattering is rather low, as it is a weak two-photon process, with only 1 in 10^7 incident photons being scattered. Apparently, the experimentalist has, in regard to the equation above, control only over the laser intensity in enhancing the signal. This reality took quite a turn in 1974, when a team of scientists discovered Surface Enhanced Raman Spectroscopy (SERS) at the University of Southampton. Fleischmann et al. observed a million fold increase in the spectra of adsorbed pyridine on a roughened silver electrode³⁸. Three years later, Albrecht and Creighton³⁹, and independently van Duyne and Jeanmarie⁴⁰ published their work attributing the SERS effect to localized electromagnetic fields at the studied electrode surface, in both cases roughened silver. The enhancement was far larger than what one would have expected from the increase in surface area of the roughened electrodes. As this effect was discovered experimentally, many theories have been proposed, with many still under debate even 40 years after its breakthrough. All theories have been narrowed down to two main contributing factors: the electromagnetic enhancement (EE) already suggested in 1977 and the chemical enhancement (CE)⁴¹. The larger EE, yielding an enhancement factor (EF) of $10^4 - 10^8$, is a non-adsorbate specific enhancement due to the focusing of the electric field at the metallic surface via plasmon resonance. The field is increased causing the surface to bathe in a freely moving electron cloud that intensifies the polarization. For a metallic sphere approximation, an enhancement factor would multiply the original field expression:

$$E_r = E_0 \cos \theta \left[1 + g \left(\frac{a^3}{r^3} \right) \right]$$

where E_r is the total electric field at a distance r from the sphere surface, a being the sphere radius, θ the angle relative to the electric field direction, and g a constant related to the dielectric constants ε_1 and ε_0 of the metal sphere and the medium surrounding it respectively:

$$g(\omega) = \left(\frac{\varepsilon_1(\omega) - \varepsilon_0}{\varepsilon_1(\omega) + 2\varepsilon_0} \right)$$

g will take a maximum value when $\varepsilon_1 = -2$, as ε_0 is usually close to 1, making coinage metals very good enhancers⁴². Under these conditions, the electric field is greater perpendicular to the surface than parallel to it, and drops significantly moving away from the surface as it is inversely proportional to the cube of the distance. It is experimentally known that the main enhancement occurs at the contact point of two spheres and not evenly around, where the junctions act as lightning rods or hot spots, becoming extremely active with the appropriate laser frequency. For small frequency shifts, one speaks of a “fourth power of field enhancement” or simply E^4 , as both incident and scattered light can be in near resonance with the plasmon frequency.

When molecules adsorb to the surface however, their symmetry changes depending on the orientation with which it is attached. This is a useful tool to possibly determine the orientation of adsorbed molecules from SERS spectra, as different modes will reflect the modified symmetry. Adsorption of molecules on a transition metal surface implies a dynamic donation of electrons from a bounding molecular orbital to the metal d-band and back to the adsorbate. This donor-acceptor mechanism can play a role in the chemical enhancement (CE) mechanism⁴³. The CE, or charge transfer (CT) enhancement, contributes a smaller enhancement factor, arising from the chemisorption of the adsorbate at the metal surface, due to charge transfer from metal to adsorbate (analyte) and back to the metal⁴⁴. The bond formation between the two creates new electronic states and therewith increases the molecular polarizability. The SERS signal is strongly dependent on the adsorbate nature and the potential applied at the

electrode. The signal observed from the CE depends on the charge transfer mechanism and leads to enhancement factors of $10^2 - 10^4$. Experimental as well as theoretical studies have, however, suggested that the EF could be actually much larger^{45,46}. Two main processes have been suggested for possible SERS charge transfer: the first (*cf.* Figure 3.2 (a)) suggests that upon plasmon absorption, an excited electron is transferred directly from the metal to the adsorbate. As for case (b), the mechanism is somewhat different, where the transition happens in the adsorbate (*cf.* Figure 3.2 (b)), only reducing the required energy for pathway (1), as the metal acts as an intermediate, redirecting the transfer via pathways (2) + (3).

Figure 3.2 Energy diagram for a possible SERS mechanism with charge transfer (a) an electron is transferred from the metal directly to the adsorbate upon plasmon absorption, (b) the metal acts as a charge transfer intermediate, reducing the transition energy – inspired by³⁵

Not only coinage metals like Au or Ag are suitable for SERS, but transition metals as well. The SERS technique has been demonstrated by Tian et al. on a number of transition metals as they improved and extended the original roughening method⁴⁷. Designing a surface with an ideal morphology for the optimal SERS enhancement is not an easy task. Roughened electrodes using oxidation and reduction cycling (ORC) that have been fabricated 40 years served quite well, but the need for a higher reproducibility has challenged experimentalists to design new, structured templates that fall in two categories: colloidal substrates and rationally designed arrays. Concerning colloidal substrates, the aggregation of metal NP is the primary condition of using them for SERS applications. It has

been shown for Au, Ag and Pt suspensions mainly in biological experiments where the NPs can be injected into live cells to obtain certain spectral information. Rationally designed arrays, and as the name suggests, are substrates that have regular, repetitive nanofeatures that are highly reproducible. Nanorings, nanorods, nanotriangles, nanoflowers, nanopits and nanotip arrays are just a few of the new systems in the SERS community.

A rather simple ingredient has been essential in fabricating reproducible arrays in the submicron range: polymer nanospheres. The metal film over nanosphere (MFON) was one of the first completely reproducible SERS substrates⁴⁸ as the polymer template allows control over the sphere size and metal film thickness, resulting in enhanced Raman signals when matching the sphere diameter to the incoming laser wavelength. This is also valid for *in-situ* measurement where the intensity drops by a factor of n^4 for a medium with a refractive index n ⁴⁹. Even though MFON substrates are tunable to some degree, combining nanosphere lithography with metal electrodeposition can create hexagonal arrays of spherical nanovoids, where sphere size and film height are independently tuned for better resonance with the excitation wavelength. The latter approach is known as the sphere segment void (SSV) technique and has been intensely developed in Southampton by Bartlett et al.⁵⁰, who used metal salts to deposit Pt, Pd and Co films through submicron polystyrene spheres (PS). A detailed description of the fabrication procedure will be given in Section 4.1, where the SSV is the photoanode support upon which the semiconducting photoactive metal oxide is anchored.

3.3 Plasmon Modes

A plasmon is defined as the collective oscillation of electronic charge on the background of fixed (positive) ionic charges in a metal. A surface plasmon refers to charge fluctuation at the metal-dielectric interface. When coupled with an electromagnetic wave (e.g. from a laser), the surface plasmon enters an excited state resulting in a surface plasmon polariton (SPP). The latter cannot be

generated on a flat surface due to a momentum mismatch between incident photons and surface plasmons present at the interface⁵¹. There are several ways in which this mismatch could be corrected for, one of which is using a prism for coupling, another by scattering off surface nanodefects or off diffraction gratings such as those provided by the SSV structure^{49,52}. SPPs have a combined electromagnetic wave and surface charge character (*cf.* Figure 3.3 (a)). The wave decays exponentially across the interface (*cf.* Figure 3.3 (b)) making the plasmon pin to the metal-dielectric boundary. The momentum mismatch is seen in the frequency dispersion curve (*cf.* Figure 3.3 (c)) where the SP has a larger momentum than a free space photon: $k_{sp} > k_0$ ⁵².

Figure 3.3 SPP properties (a) combined electromagnetic wave and surface charge character (b) normal field component decay above the surface and in the metal (c) frequency dispersion curve of a surface plasmon (dashed line) in comparison with that of a free photon to highlight the momentum mismatch – based on⁵²

Submicron-patterned metallic SSV structures possess periodically ordered cavities that facilitate the coupling of radiation with the surface plasmons. The complex morphologies are fabricated by electrodeposition onto a packed layer of polystyrene spheres. Throughout this thesis, the structure of the SSV is specified in terms of its thickness related to the sphere diameter D . According to this terminology, a $0.5D$ thickness means that the film grown in between the PS reaches half the diameter of the sphere template.

A hexagonal array of shallow dishes is formed at thicknesses $< 0.3D$ where the modes generated have the ability to scatter multiple times at the rims, in a manner reminiscent of Bragg diffraction. They are delocalized anisotropic plasmons (*cf.* Figure 3.4 (red)) and can travel surface distances up to several microns. As Bragg plasmons only appear on relatively flat surfaces, they

disappear for thicknesses higher than $0.3D$ and reappear at $0.75D$ where “necks” are formed between the closely packed PS. The modes that appear as the shallow dishes grow into spherical voids at thickness above $0.3D$ are the localized Mie plasmons trapped into a spherical void. When the SPP is reflected in the isotropic void (*cf.* Figure 3.4 (blue)) it will interfere with itself forming a localized mode, often referred to as localized surface plasmon or LSP, that is independent of the incident light angle⁵³.

Figure 3.4 Approximate plasmon location on an SSV substrate ($0.75D$) Delocalized surface Bragg plasmon modes propagate on the top (red) and the localized Mie plasmons are confined within the spherical voids (blue) – based on⁵¹

At certain film thicknesses, mixed plasmons start to be observed (*cf.* Figure 3.5) due to the interference of Mie and Bragg plasmons. As the thickness increases from $0.2D$ to $0.3D$, the modes become stronger now that the cavities are more pronounced. After $0.39D$, and as the surface breaks into disconnected triangular islands, the Bragg mode splits into higher and lower energy modes, which indicates as expected, the excitation of Mie plasmons of comparable energies, independent of incident angle. The contribution of Bragg plasmons can be tuned by the sphere size, as they are highly dependent on periodicity, and that of Mie plasmons by tuning the film height along with the sphere size to enhance the localized field.

Figure 3.5 Reflectance spectra with respect to incident angle for four different film thicknesses up to $0.39D$ using a $D = 500$ nm Au SSV array. The intensity of the reflected beam is plotted as a function of the angle of incidence and of light quanta energy (wavenumber). Color code: higher intensity is blue, lower intensity is red. Red areas indicate energy loss from the incident beam due to plasmon excitation.⁵⁴

Experimentally, SSV substrates reveal many modes which cannot be really identified to either Bragg diffraction or Mie modes. This is first due to the fact that calculations are done for a single, isolated void in contrast to experiments, which can be carried out on multiple arrays. It is also due to the complexity of the mixed modes such as the presence of a third, hybrid mode called the rim mode, due to charge build up at the void rim, especially at high thicknesses.

4 Experimental Methods

4.1 Substrate Preparation

The SERS substrate used here is the thoroughly-studied nanovoid substrate (SSV) that has been developed at the University of Southampton more than one decade ago^{55–61}. Au nanocavity arrays can be produced with various sphere diameters, ranging from few hundred nanometers up to a few microns. Of major interest are spheres of sizes 500 to 800 nm due to their ability of being tuned with laser wavelengths in the optical range. Cavity heights grown from $\sim 0.1D$ to $\sim 0.9D$ show that up to a height of $0.4D$, the film or top surface has a relatively large area between the cavities, after which they decrease, and become interconnected at locations where the spheres initially touched⁶². At this thickness, the top surface breaks into connected triangular sections, which is used as a base for the interconnected TiO_2 pillars, as will be explained in section 4.2.

The preparation could be described as follows. Microscope glass slides were thoroughly cleaned in isopropanol and acetone in an ultrasonic bath and dried in a nitrogen stream. They were then transferred to a vacuum chamber to be coated with an adhesion layer of Ti (10 nm) followed by a Au film (200 nm). They were then partitioned into pieces of 25×25 mm using a commercial diamond cutter, and a hexagonal parafilm mask was applied to each piece to enhance radial solution evaporation and finally sealed by a glass cover slip (*cf.* Figure 4.1 (step 1)) to form an impermeable pocket of $\sim 100\text{ }\mu\text{m}$ thickness through which the polystyrene sphere suspension was filled (step 2). Sealing the pocket was completed upon placing all components on a heating plate at around 70°C and pressing until the parafilm changed from translucent to slightly transparent, confirming the adhesion. The pocket was then filled with $\sim 10\text{ }\mu\text{L}$ of the aqueous 1% wt PS solution using a micropipette, after shaking it vigorously to ensure a

homogeneous suspension (step 3). Samples were then placed in an incubator at 14°C for 72 hours in holders inclined at a 15° angle. These conditions ensure a slow constant evaporation rate to form a well-packed template by the convective assembly method ⁶³. When the solvent level drops below the sphere diameter, the capillary forces at the liquid-air interface lead to attractive ones between the PS resulting in a highly-ordered sphere packing (step 4) ⁶⁴.

Figure 4.1 Preparation steps of an SSV substrate ⁴⁹

After the incubation period, the cover slip and parafilm were carefully removed by reheating the system on the plate at 70°C, which is the temperature chosen to avoid the PS from being burst or deformed. The active area was isolated from the rest of the gold slide with commercial transparent nail polish for the subsequent electrochemical deposition through the polystyrene template. The deposition was performed in a mixture of 45 mL Au electroplating bath ECF 60 (Metalor), and 225 µL brightener solution E3 (Metalor), not only for a smoother finish but also for the optimization of nucleation and deposition kinetics (step 5). Using a standard

three-electrode setup, with the glass slide as working electrode, a Pt mesh as the counter electrode, and a Standard Calomel Electrode (SCE) as reference, the deposition potential was set to -720 mV using a potentiostat. The progress of the Au deposition was monitored by the charge flowing through the working electrode by recording in chronoamperometric mode. According to Faraday's Law^{65,66}:

$$Q = \frac{n\rho AF}{m}H$$

where Q is the total charge passed through the electrode, n is the number of moles involved in the reaction, A the area of the active electrode deposition site, ρ the density and m the molecular mass of Au, F the Faraday constant and H the height of the film, limited to fractions of the diameter D , in the notation $H = 0.xD$ as discussed before in section 3.3 ($D = 500/600$ nm in this work).

A typical transient curve consists of three regions (*cf.* Figure 4.2), where region (A) corresponds to monolayer Au formation with instantaneous nucleation, (B) to successive Au monolayer formation with progressive nucleation and (C) to a three dimensional nucleation and growth process. The surface area reaches a minimum for a film thickness equal to the sphere radius, where the inter-spherical distance is minimal, and is denoted by $0.5D$ shown as a peak in region (C). This reference point was used for depositing Au at different heights by setting:

$Q_{0.5D} = CH = C(0.5D)$ using the above equation, where $Q_{0.5D}$ is the charge necessary to deposit a layer of thickness $D/2$. This charge can be easily determined, since the deposition current presents a maximum there. The constant C consists of $\frac{n\rho AF}{m}$, hence:

$$\frac{Q_{0.xD}}{Q_{0.5D}} = C \frac{0.xD}{0.5D}$$

To give a simple interpolation/extrapolation factor of 2 for $Q_{0.xD} = 2(0.x)Q_{0.5D}$

After deposition, the polystyrene spheres were removed by dissolution in Dimethylformamide (DMF) after a treatment of few hours.

Figure 4.2 A typical chronoamperogram obtained upon depositing Au at -720 mV vs. SCE onto a $D = 600$ nm sphere template⁵⁴.

4.2 TiO₂ Synthesis by Chemical Bath Deposition

In the field of surface science related to transition metal oxides, TiO₂ is probably the most investigated metal oxide system due to its importance in a wide spectrum of applications such as heterogeneous catalysis, optical or corrosive protective coatings, disinfection mechanisms and most notably in solar energy applications. TiO₂ crystallizes in three major structures: anatase, rutile and brookite with the first being the most widely used polymorph for PEC purposes commonly in the alkaline region due to the flat band potential shift (section 2.4) and thoroughly described by Fujishima et al.⁶⁷. An enhanced charge separation hinders recombination processes and enhances the charge transfer kinetics.

Among many methods of synthesizing TiO₂ thin films is anodization, thermal oxidation, chemical vapor deposition, sputtering and chemical bath deposition

(CBD) from aqueous solutions^{68–70} which will be discussed here. TiO₂ was synthesized using a peroxo complex of titanium in the presence of HCl at low temperatures⁷¹. The need of an anchoring agent between the TiO₂ and the SSV substrate led to modifying the Au substrates in a 2.5 mM solution of Mercaptoundecanol (MUO) for three hours, after which they were thoroughly rinsed and dried with N₂ before performing the metal oxide deposition⁷². The Self Assembling Monolayer (SAM) solution improves the adherence of TiO₂ to the underlying substrate, without which it will be unstable. Many tests were done in the laboratory on both silicon wafers and SSV substrates, with and without the SAM. Without this layer the metal oxide will peel off upon slightest contact with the electrolyte, even after high temperature annealing.

The preparation of the stock Ti-peroxo complex $\text{Ti}(\text{O}_2)^{2+}$ was carried out in an ice bath due to the exothermic nature of the involved mixing reactions. Fresh TiCl₄ was added drop-wise to the ice-cold solution of H₂O₂, stabilizing thus an otherwise rapidly precipitating aqueous titanium solution, and diluted with ionized water to a 10 mM solution. The SAM-modified samples were then immersed in a mixture of stock solution and 10 mM HCl at 70°C for two hours (concentrations ranging from 1 mM to 150 mM were also tested). The HCl concentration was adjusted around the deposition temperature, as higher deposition temperatures demand higher HCl concentrations. Very low HCl concentrations lead to visible bulk TiO₂ deposition, while no deposition occurred at extremely high concentrations.

It is worth noting that the average deposition rate is ~50 nm/h for a static deposition as performed here. For deposition times longer than two hours, the rate increases rather parabolically than linearly, calling for a liquid flow deposition. The latter was imitated for longer test depositions by changing the solution midway and replacing it with a fresh one. The samples were then thoroughly rinsed and sonicated in a warm bath for 10 minutes to remove any residual agglomerates. Ramp annealing with a rate of 4°C/min was used to induce crystallinity in the formerly amorphous TiO₂ at temperatures ranging from 450°C to 650°C. The samples were then left to cool down properly to avoid any bending, rinsed, dried with N₂ and stored until measurement.

4.3 Atomic Force Microscopy (AFM)

After carrying out the deposition process on the SSV substrates, it goes without saying that a characterization method is necessarily called for. A common method that can be used for many types of substrates, even non-conductive ones, is atomic force microscopy (AFM), an imaging technique based on the interactions at the atomic level between the sample to be examined and a sharp tip. This tip is mounted on a so-called cantilever (*cf.* Figure 4.3 (a)) which is driven to oscillate at its natural frequency by piezoelements. An incoming laser beam, which is reflected to a photodiode, produces a sinusoidal electric signal. The sharp cantilever tip moves over the surface until the cantilever itself bends consistently with the surface forces, while the position-sensitive photodiodes record the resulting changes of the reflection spot. The positioning and scanning movement of the cantilever, laser and photodiodes is affected by the x- and y-piezoelements. The signal recorded by the photodiodes goes to the z-piezoelement that moves the cantilever along the z-direction, compensating for vertical obstacles on the surface and assembling the measured deflection data into a topographic image of the surface.

AFM can operate in three different modes: contact mode, non-contact mode and tapping mode. The latter has the advantage that the contact time between sample and tip is reduced resulting in a non-destructive measurement (*cf.* Figure 4.3 (b)), in addition to significantly reducing difficulties caused by friction and adhesion⁷³. In tapping mode, the AFM tip oscillates between distances of contact and non-contact (*cf.* Figure 4.3 (c)) intermittent by the force exerted on the AFM tip being of the type of the Lennard-Jones potential curve, which is related to the distance d as follows:

$$U(d) = 4\varepsilon \left[\left(\frac{\sigma}{d} \right)^{12} - \left(\frac{\sigma}{d} \right)^6 \right]$$

Measurements shown in Section 5.2.3 were recorded in air with AFM (Veeco) and RTESPA cantilevers (Bruker), and all analysis (of which height profiles) was completed using the software package NanoScope Analysis (Veeco).

Figure 4.3 AFM operation mode (a) laser reflection on cantilever to photodiode (b) advantageous non-contact over contact mode (c) Lennard-Jones potential and mode distribution – based on 74,75

To further check the wetting properties of the SSV substrate, shown in Section 5.2.4, another important application of AFM was used: Force Spectroscopy. The cantilever is pushed into the sample and subsequently retracted resulting in a so-called force-distance curve since the deflection is related to the force applied by the tip on the sample. Of the piezoelements mentioned before, it is the z-piezo which processes the height information and sends it to the photodiode which also detects the cantilever's vertical deflection. Each scan creates two curves for approaching and retracting the AFM tip, that describe the deflection as a function of height. Whilst approaching the sample *i.e.* the trace curve, the cantilever is moved without touching the sample (*cf.* Figure 4.4 (1)) where no adhesion occurs until the cantilever is suddenly attracted to the sample giving a small deflection (2) also known as the point of “*jump to contact*”. By pushing the cantilever further down, it is bent upwards in a way proportional to the piezo height (3). This linear slope is very significant for cantilever calibration. The cantilever is then withdrawn after reaching a defined deflection setpoint (4). It unbends while moving away from the sample (5) while still experiencing adhesive forces causing it to bend in

the opposite direction losing contact (6) and returning to its original position. Retracting the cantilever further no longer causes any deflection depicted in the straight line (7).

Figure 4.4 A typical force-distance curve for approach and retract modes – based on ⁷⁵

The cantilever's characteristic properties like spring constant k and sensitivity s are known, enabling the calculation of the force applied by multiplying them by the deflection u , $F=ksu$.

The force-distance curves in Section 5.2.4 were performed in four different media: air and three solutions, using a Nanoscope (NanoSurf) setup and analyzed with C3000 (Nanosurf) controller software. For air, water and ethanol, cantilevers of type TAP190Al-G (NanoAndMore) were used, but not in NaOH, as the aluminum oxide layer was dissolved. A cantilever TAP190-GD was used instead, allowing recording a required noise-free signal.

4.4 Scanning Electronic Microscopy (SEM)

In a scanning electron microscope (SEM), electrons are used as probe particles for the analysis of surfaces on the nanometer scale. It is possible to obtain different qualitative and quantitative information from the sample, depending on

the type of radiation detection. An electron beam of energy ranging between 0.2 to 40 keV is focused by condenser lenses to a spot of 0.1 to 5 nm diameter and emitted from the electron gun onto the sample. The electron beam then loses energy by combined processes of absorption and scattering within the so-called interaction volume. This is a pear-shaped domain within the sample (*cf.* Figure 4.5) which can extend up to few microns depth. Secondary electrons scattered inelastically near the incident beam are suitable for topographical imaging. They are low energy electrons resulting from multiple collisions with substantial energy loss, or by the ejection of loosely bound electrons in the sample. The latter are detected with a scintillator type detector which is positively charged and improves signal to noise ratio. This type of detector could also be used for detecting backscattered electrons, which are of higher energy in comparison to that of incident electrons, that are ejected by elastic collisions deeper in the sample volume.

Figure 4.5

Various signals emitted from different sections within the interaction volume – based on ⁷⁶

Another variety of emission upon interaction with an electron beam results from the removal of core electrons. Upon the ionized atom's relaxation to a lower energy state by the transition of an outer-shell electron to the vacancy in the core shell, a characteristic X-ray is emitted. This phenomenon is exploited to perform elemental analysis, mapping the composition and abundance of elements in the sample, and is referred to as energy-dispersive X-ray spectroscopy (EDX/EDS). It is a rather sensitive technique since the radiated X-ray quanta can be assigned to one specific element depending on the difference in the energy levels (typically K, L and M levels) involved in the transition^{77,78}.

4.5 Wavelength-dependent Photocurrent

For wavelength-dependent measurement investigations, a self-mounted experimental setup was used (*cf.* Figure 4.6) consisting of an optical bench fixated on an M6 laser table with a 450 W ozone-free xenon lamp (Newport) with housing and power supply (Oriel Instruments). The beam was focused to harvest the maximum intensity with plano-convex lenses, one at the entrance, and two at the exit of a motorized monochromator (Newport). A precision long pass filter (Edmund Optics) with blocking range of 200 - 390 nm, and transmission range of 408 - 1650 nm was used in calibration measurements to exclude eventual stray light effects in the resulting photocurrent. The cell used is a standard three-electrode electrochemical cell (Zahner) equipped with a quartz window. Measurements were carried out in 0.1 M NaOH electrolyte, at 0 V using Ag/AgCl reference electrode and a Pt counter electrode.

Figure 4.6 Experimental setup used for wavelength-dependent measurements, with (1) xenon lamp, (2) monochromator and (3) electrochemical cell

The optimal position of highest intensity where the cell was placed, was determined with a photodiode (Newport 818-UV-L) also used to measure the power curve $P_{\text{light}}(\lambda)$ (will be highlighted in Section 5.3.1) needed for IPCE calculations Section 2.5.

$$IPCE(\lambda) = 1240 \left(\frac{J_{\text{photo}}(\lambda)}{P_{\text{light}}(\lambda)\lambda} \right)$$

4.6 Solar Simulator

A solar simulator, also known as “artificial sun”, is a device that provides illumination approximating natural sunlight. The purpose of the solar simulator is to provide a controllable indoor test facility under laboratory conditions, used for the testing of solar cells, plastic and other materials. The simulator used for measurements is a AAA-class type (HelioSim-CL60, Voss Electronics) with a near AM 1.5 spectrum (*cf.* Figure 4.7). The Air Mass (AM) coefficient syntax has become the standard representation of irradiation conditions, where the number following the syntax is defined as the secant function of the zenith angle. According to this notation, AM 1.5 correlates to a zenith angle of 48.2° representing the international average of 1 Sun equal to 100 mW/cm².

As the simulator contains glass optical components, its emission spectrum begins at around 370 nm, hence the near AM 1.5 classification. Similarly, measurements were carried out in the same cell, in order to work under same electrolyte depth conditions in 0.1 M NaOH. Photocurrents measured were calculated as the difference between light and dark currents generated upon chopping the light beam by using the solar simulator’s built in shutter.

Figure 4.7 Solar Simulator spectrum (blue) compared to AM 1.5 natural solar spectrum (red)

4.7 Cyclic Voltammetry (CV)

One of the most widely used electrochemical methods present is cyclic voltammetry (CV) providing information on catalytic, kinetic and thermodynamic properties at the electrode surface. A stationary working electrode is brought in contact with a static electrolyte, whilst an initial potential U_i , measured against a stable reference electrode (RE) is set by a potentiostat. The potential is subsequently swept between two defined reversal points U_A and U_B within the stability domain of the electrolyte. In aqueous electrolytes, hydrogen evolution at negative potentials and at more positive ones oxygen evolution, mark the limits of that domain. The electrode potential is customarily swept at a constant rate between U_A and U_B giving the voltage's triangular waveform. The current recorded then flows between the working electrode (WE) and a third electrode, the counter electrode (CE), and is usually plotted as a current density by normalizing the absolute current to the geometric area of the WE. This three-electrode arrangement used throughout this work, has the advantage that the reference electrode, held at a minimal distance from the working electrode to reduce ohmic losses in the electrolyte bulk, plays an observer role regulating the applied potential so it doesn't get influenced by any electrochemical reactions. Prior to each measurement, electrolytes were usually purged with nitrogen that

displaces the solvated oxygen and hinders the otherwise occurring electrochemical oxygen reduction at more positive potentials.

4.8 Raman Characterization and EC-SERS

The Raman setup used throughout this work is of dispersive type, involving a diffraction grating and mirrors for light dispersion and selection of suitable wavelengths. A dispersive spectral analysis system has many advantages over a Fourier Transform (FT) Raman system due to its working in the visible domain to optimize scattering properties for a wide range of samples by enhancing sensitivity, offering better control of penetration depths and focusing fluorescence rejection. Other than providing a diffraction-limited spatial resolution of 1 micron via the confocal Raman microscope, it offers high flexibility in solving issues related to fluorescence of samples, by supporting multiple excitation wavelengths from far UV (244 nm) to near IR (830 nm). This helps analyze inorganic samples and biomolecules even in aqueous solutions, which is hindered by the use of Nd:YAG 1064 nm FT Raman system.

The spectrometer used in this work is an In Via (Renishaw) (*cf.* Figure 4.8) Raman dual-laser system encompassing a Leica DM 2500 microscope with different objectives ranging from 5× to 150×. Both the He-Ne laser (633 nm of 17 mW power) and a frequency-doubled Nd:YAG laser (532 nm of 50 mW power) were used to analyze the SSV substrates and study the plasmonic resonance in air (N PLAN EPI 50×/0.75 objective, Section 5.4.1) and under electrochemical conditions (HC PL FLUOTAR L50×/0.55 long-distance objective, Section 5.4.2).

Figure 4.8 Renishaw InVia Raman Spectrometer block schematics

The laser beam entering the system via the back of the spectrometer at mirror (a) is aligned and focused into concentric circles via the beam expander (b) which is equipped with a pinhole. It is then redirected to the microscope, where the sample is viewed through the integrated objective, via the adjustable mirror (c). Filter (d) receives the Raman and Rayleigh scattered light that is reflected back through the microscope, filtering the dominant Rayleigh scattering and any other stray light to allow only Raman scattered light to fall on filter (e), set to width to channel the maximum light through the post adjustable slit (f). The latter refocuses the light onto collimator (g) and subsequently grating (i) with 1800 grooves/mm (633 nm) or 2400 grooves/mm (532 nm) using the wedge mirror (h). The scattered light is focused through lens (j) onto the highly-sensitive charge coupled device (CCD) detector (k).

The system was calibrated using a silicon wafer reference before every measurement, its peak occurring at 520.5 cm^{-1} and offsetting the grating at any variation. All spectra in air have been taken in Static Mode with 1 - 5% laser power focused at 770 cm^{-1} for quick measurements lasting few seconds where the grating remains in one position throughout the signal accumulation. The so-

called Extended Mode was used for electrochemical SERS measurements, since a wider spectral range had to be made available by moving the grating and setting minimum acquisition time to 10 seconds. The latter have been carried out in a self-designed cell ⁷⁹ with a standard calomel electrode as a reference electrode and a platinum wire as counter electrode immersed in ~ 500 μ L electrolyte. The working electrode was connected through a contact spring, isolated with an O-ring from the electrolyte. Chronoamperometric measurements using a potentiostat were set to control the applied potential while accumulating the corresponding Raman spectra at the constant set potential.

4.9 Materials

Table 4.1 List of materials used

Chemical / Material	Supplier	Purity
Acetone	Merck	99.9%
APTMS	Sigma Aldrich	97%
Au (111)	MaTeck	99.9999%
Brightener E3	Metalor Technologies	As received
Concentrated Sulphuric Acid	Merck	96%
Cover Slips	VWR	Technical
Deionized Water	Merck	TOC < 3 ppb
Dimethylformamide	Merck	99.9%
Ethanol	Merck	99.9%

Gold Electroplating Bath ECF 60	Metalor Technologies	As received
Gold wire	MaTeck	99.999%
Hydrochloric Acid	Merck	30% Suprapur
Hydrofluoric Acid	BASF	50% Selectipur
Hydrogen Peroxide	Merck	35%
Isopropanol	Merck	99.5%
Mercaptoundecanol	Sigma Aldrich	97%
MPTS	Sigma Aldrich	> 80% - Technical
Nitrogen Stream	MTI	99.999%
Parafilm	Bemis	Technical
Platinum Gauze	Goodfellow	99.9%
Polystyrene Spheres (500 nm, 600 nm)	Thermo Fischer Scientific	1% wt
Sodium Hydroxide Pellets	Merck	99.9%
Sodium Metasilicate	Sigma Aldrich	44 - 47%
Titanium Tetrachloride	Fluka	99.9%

5 Characterization of Metal-doped Photoanodes

5.1 Research Aims and Thesis Overview

Experiments involving Au nanoparticles evaporated onto a TiO_2 substrate demonstrated the crucial role of Au in the photoreaction⁸⁰. Under visible illumination, and due to plasmonic effects, a 66-fold enhancement in the photocurrent has been observed in the presence of Au nanoparticles in comparison with the bare TiO_2 photoanode. Plasmon-induced photoelectrochemistry was intensely studied in gold nanoparticle-nanoporous TiO_2 composites^{81,82} as well as on gold-modified powders⁸³, showing significant peaks of the photoresponse in the visible range. This is due to the localized surface plasmon resonance (LSPR) in Au nanoparticles, which occurs in the range of 530 - 620 nm, depending on the nanoparticle size and distribution, in comparison with surface plasmons for films that have a non-radiative electromagnetic mode⁵². As for the complementary case of a metal oxide on a metal surface, intensive research has been done on what is known as metal oxide nanoparticle enhanced Raman scattering (MONERS)⁸⁴. It demonstrates that the Raman effect can be significantly enhanced just by placing metal oxide nanoparticles (MONP) on metallic surfaces, where the MONPs are non-plasmonic themselves but induce additional functionalities to the system through their optical effects, as they are of a higher refractive index than the substrate.

By designing a new photoanode of a type which has not been investigated before, consisting of a nanostructured surface of TiO_2 deposited on a plasmonically active Au co-catalyst, it is aimed at enhancing both the Raman effect of the incoming light due to the optical properties and plasmon resonance of this ordered morphology, as well as enhancing the photo-response of the TiO_2

anode in the visible region due to the underlying Au support. It is intended to optimize this effect by addressing both factors mentioned in Section 3.2: the chemical and electromagnetic enhancements.

As the chemical enhancement deals mainly with the interaction between substrate and adsorbed molecules, it predicts a more effective enhancement on a rough surface, as the film peaks provide a route for the hot electrons to the adsorbed molecule, as discovered by Fleischmann et al.³⁸. Regarding the electromagnetic enhancement, which deals primarily with the change in the local electric field causing a strong surface polarizability, a significant phenomenon should be taken into account. It is the overlap of the incident radiation wavelength, scattered radiation wavelength, and a surface plasmon resonance characteristic of the substrate, with the latter being simply defined as the surface excitation of electron-hole pairs: the quanta of oscillation of the surface charges of a metal at a certain frequency, produced by an external electric field.

In the system studied in this work, TiO₂ pillars are grown on a SERS active Au SSV substrate, where they mimic the photoelectrochemical behavior of TiO₂ nanotubes, acting as antennae to couple the incoming light absorption while feeding on the plasmonic effects of the underlying SERS substrate. The advantage of the SSVs negative curvature confinement is the increase in plasmon energies due to a larger field overlap coupled to external photons in the well-defined cups which are tunable from UV to NIR⁶⁰. The fields are concentrated in the cavity as opposed to around a NP resulting in another advantage being reduced damping in the SSVs. The extended plasmon lifetimes is an outcome of reduced optical losses, due to re-radiation within the void, and reduced absorption loss, due to reduced damping as opposed to regular AuNP.

The enhancement on such a surface is due to coupling of the metallic nanoparticles' LSPR and the propagating SPP of the smooth metallic substrate at the bottom of the void. Previous works demonstrated that optimal SERS signals using a 633 nm laser were obtained for benzene-thiol adsorbed on SSV substrates using $D = 600$ nm diameter PS, in which the deposition height was $0.8D$, *i.e.* a height of 480 nm^{85,86}. The size of the surface cavity was 480 nm with

an inner diameter of 600 nm. This is very suitable for enhancing visible light absorption and matching the Au-LSPR, as it has been shown that when the laser wavelength is comparable with the size of the particle under investigation, the strongest SERS signal is observed^{85,87–89} as will be demonstrated here.

5.2 Sample Structure and Composition

5.2.1 TiO_2 layer on p -Si substrate

As mentioned briefly in Section 4.2, the first deposition attempts were made on p -type silicon wafers, which were sliced with a diamond pen, cleaned thoroughly in ultrasonic baths of acetone, ethanol and deionized water. The etching in hydrofluoric acid was skipped after thorough testing, as the native oxide layer present on the wafer improved adhesion of the TiO_2 layer after deposition. This layer is seen in the SEM image (*cf.* Figure 5.1) after a 4 hour deposition, almost 200 nm thick, which correlates to a ~ 50 nm/h deposition rate. The quality of the oxide layer is comparable to those obtained by UHV sputtering techniques, but the present preparation route is more convenient.

Figure 5.1 Cross section SEM image for a TiO_2 film on a p -type silicon wafer (left) and EDX analysis (right). Region (1) consists of TiO_2 , region (2) is silicon.

5.2.2 TiO_2 layer on SSV substrate

The first substrate shown here $D = 600$ nm with $0.8D$ deposition height has been well studied by the group of Bartlett in Southampton⁶². In Figure 5.2, a clear SEM picture of the top surface, broken at this deposition height into connected triangular sections, is seen with the line profile (right) confirming the actual height. Considering the sphere geometry, the uppermost diameter should have a theoretical value of 480 nm, which fits well with the value of 495 nm estimated from the figure.

Figure 5.2 SEM image of the Au array using $D = 600$ nm diameter spheres with deposition height $0.8D$ (left). Close-up image including a line profile, marked in red (right)

The first method, designated Method “A” for growing pillars on the SSV structure entails depositing the TiO_2 on top of the PS before dissolving them, followed by annealing to dissolve the spheres (stable till only 89°C) leading to a pillared structure formation at the points where the cavities are connected. This recipe unfortunately did not work out as planned, since the entire TiO_2 film (deposited for 4 hours) experienced a lift-off, exposing the SSV. This could be compared to a MFON method, as seen in the SEM image in Figure 5.3 on the right.

Figure 5.3 Illustration of Method "A" (left) and the resulting TiO_2 film structure which peels off the SSV substrate upon annealing as seen in the SEM image (right)

The second method designated Method "B" consists of filling the cavities in the attempt to form truncated spherical TiO_2 structures. The metal oxide was deposited after dissolving the spheres in DMF. The SEM image in Figure 5.4 (right) shows that filling of the cavities was not quite achieved and an interesting pattern corrugating the interconnected Au triangles underneath is observed instead. This was later attributed to the hydrophobicity of the cavity surfaces. The deposition was carried out for 4 hours, hence the time was reduced to 2 hours as not to seal the SSV cavity structure completely.

Figure 5.4 Illustration of Method "B" (left) and the resulting TiO_2 structure as seen in the SEM image (right). The corrugation of the texture corresponds to the SSV substrate periodicity.

For $D = 600$ nm spheres and low deposition heights of $0.3D$, deep cavity formation is very improbable, thus leaving only relatively open voids (*cf.* Figure 5.5 (a)). Therefore, after the TiO_2 deposition, a thin film is formed covering the underlying Au (*cf.* Figure 5.6 (top left)). As for all other heights between $0.4D$ and

0.9D (exemplary shown in Figure 5.5 (b,c)) the Au deposition creates a translationally symmetric cavity structure. TiO_2 deposits on the rims of these cavities due to the difference in hydrophobicity between the evaporated Au and that deposited electrochemically induced by controlling the surface topography⁹⁰ (for details see Section 5.2.4). Hexagonal tube-like pillars of TiO_2 exposing the uncovered underlying layer of Au are the result of the deposition (*cf.* Figure 5.6).

Figure 5.5 3D model using Inventor Software to simulate the expected Au structure before TiO_2 deposition for three chosen heights (a) 0.3D (b) 0.5D (c) 0.8D

EDX measurements (*cf.* Figure 5.6 (bottom)) clearly show that exposed darker areas (spectrum 3) are clear Au and that TiO_2 deposits only on rims (spectrum 1).

Figure 5.6 SEM images after TiO_2 deposition on Au SSVs with models shown as insets: Au as yellow: TiO_2 as blue (top) EDX spectra of different areas of sample (b) (bottom)

For $D = 500$ nm, the deposition process was controlled via SEM imaging, where Figure 5.7 (left) shows a close-up SEM image, highlighting the highly ordered SSV structure for the deposition of $0.5D$ through 500 nm spheres. The line profile along the red lines gives a cavity diameter of 499.5 nm, which proves yet again the accuracy of the deposition process, despite the fact that it is controlled manually. In Figure 5.7 (right), after subsequent TiO_2 deposition that takes place on the cavity rims, the homogeneous cavity structure remains unaltered.

Figure 5.7 SEM image with line profile for bare structures $0.5D$ of $D = 500$ nm (left) and after TiO_2 deposition on $D = 500$ nm spheres (right)

5.2.3 AFM investigation of the deposited TiO_2 films

Height profiles were acquired via AFM imaging as shown in Figure 5.8, where the blue plus symbols highlight the top and bottom of one of the voids.

Figure 5.8 AFM image ($5 \times 5 \mu\text{m}$) for $0.5D/\text{TiO}_2$ (left) height profile of cavity top to bottom (right)

The height profile shows a very good agreement with the theoretical height of 400 nm for voids in a $0.5D$ structure where the TiO_2 pillars are of ~ 100 nm height (also proven below by Figure 5.10). AFM height profile measurements were done for all samples to check their stability at high annealing temperatures, and they have proven to remain stable.

Figure 5.9 AFM height profiles of TiO_2/SSV for $0.3D$ (left) $0.4D$ (middle) and $0.6D$ (right)

Deposition height	$0.3D$	$0.4D$	$0.5D$	$0.6D$	$0.7D$
Expected value (nm)	280	340	400	460	520
Measured value (nm)	279	344	409	457	—

Table 5.1 Depth of the cavities on TiO_2/SSV structures determined by AFM. At $0.7D$, the cantilever tip is too large to penetrate the cavity.

Figure 5.10 Height profiles from an AFM image for an SSV cavity $0.6D$ ($D = 600\text{nm}$) with and without TiO_2

5.2.4 Force-Distance spectroscopy

The SSV's unique wetting properties were thoroughly analyzed by AFM Force-Distance measurements described in Section 4.3 in four different media in and outside the cavities. The curves in Figure 5.11 show that the cavities are not completely filled with electrolyte, since the interruption or slope change in the force-distance curves hints at the border crossing from the liquid to the air cushion lying underneath. This observation further supports the result that the metal oxide deposits only on the cavity rims and not inside them. The chemical bath deposition is performed in an aqueous solution so the wall hydrophobicity precludes TiO_2 deposition in the cavities as confirmed in Figure 5.6.

Figure 5.11 Force-Distance curves taken in four media on top and inside a clean Au SSV cavity. Movement of the AFM tip towards the sample is represented by increasing values of the relative vertical distance.

5.3 Photoelectrochemical Measurements

5.3.1 Photocurrents and IPCE ($D = 600\text{ nm}$)

IPC efficiencies are useful indications for comparison with other photoanode systems, these values being independent of light source or lamp power due to normalizing the photocurrent to the incident photon density, as described in the IPCE equation of Section 2.5. Using a photodiode, the current with respect to wavelength was recorded at the optimal position on the photo bench (*cf.* Figure 5.12 (left)) and then converted to the power curve $P_{\text{light}}(\lambda)$ (*cf.* Figure 5.12 (right)) using the photodiode's responsivity factor for 10 nm intervals from the calibration protocol (Newport) to later calculate the IPCE values.

Figure 5.12 Current vs. Wavelength recorded by photodiode 818-UV-L (Newport) (left) and the corresponding power curve (right) obtained by multiplying the current curve by that of the diode's responsivity factor (W.A^{-1})

The wavelength-dependent photocurrent measurements were carried out using the setup described in Section 4.5 for all samples annealed at 450°C , 550°C and 650°C , at all Au deposition heights. This was done in order to simultaneously study the annealing effect on the photo-absorption properties. The photospectra and their corresponding IPCE curves are summarized (*cf.* Figure 5.13 through Figure 5.15) with insets highlighting the visible range.

Figure 5.13 Photocurrent measurements (left) for TiO_2/SSV ($D = 600\text{nm}$) samples annealed at 450°C and the corresponding IPCE (right)

Figure 5.14 Photocurrent measurements (left) for TiO_2/SSV ($D = 600\text{nm}$) samples annealed at 550°C and the corresponding IPCE (right)

Figure 5.15 Photocurrent measurements (left) for TiO_2/SSV ($D = 600\text{nm}$) samples annealed at 650°C and the corresponding IPCE (right)

Due to the difference in the surface morphology for different deposition heights, as discussed in Section 5.2.2, different features can be seen in the IPCE curves. For all black curves, correlating to $0.3D$, a single peak is seen, located at around 320 nm, corresponding to the characteristic TiO_2 peak attributed to the band transition. As for all other layer thicknesses, their hybrid structure is the reason for the additional IPCE peak in the visible range, showing impressive values when compared to other systems without mediators^{81,82} (especially for samples annealed at 550°C) or for H-doped TiO_2 ⁹¹. The peak is at around 590 nm, reflecting the resonance matching the sphere diameter, and could be attributed to the LSPR of Au, which channels the induced hot electrons from the plasmonic cavities into the TiO_2 conduction band^{92,93}. The TiO_2 pillars, mimicking the behavior of nanotubes in other light-harvesting systems whilst providing a large active internal surface area, create a synergy with the plasmonic excitations (Bragg and Mie), originating in the Au sphere segment voids.

Anchoring the TiO_2 structure on top of the Au SSV substrates creates a quasi Schottky junction, which improves charge separation of electron-hole pairs created at the interface and boosts the efficiency of photocatalytic reactions under visible light irradiation. Due to the fact that the Helmholtz capacitance of the Au/electrolyte interface is much higher than the space-charge capacitance of the Au/ TiO_2 interface, the resulting effect is a shift of the Fermi level closer to the semiconductor's conduction band. This shift to a more negative potential allows the metal to stimulate an interfacial hole transfer, hindering the charge recombination process while simultaneously enhancing the photo absorption^{94,95}.

It is worth noting that the IPCE dependence on the annealing temperature is not straightforward. A significant increase is seen with the samples annealed at 550°C in comparison with those annealed at 450°C , due to a higher stability of the anatase phase, which is the most suitable for PEC measurements, since rutile is of direct whereas anatase of indirect band gap. Longer charge carrier lifetimes afford more time for participation in surface reactions. In addition, surface-bonded peroxo species are present in anatase, in contrast to their absence on rutile surfaces⁹⁶. However, for 650°C annealing, the IPCE apparently drops again, due to the fact that TiO_2 is now partially of a denser rutile form,

which is less efficient in creating long-lived electron-hole pairs, crucial for photocurrent generation⁹⁷. The nature of all TiO₂ structures has been verified by subsequent Raman measurements, which will be discussed in Section 5.4.1.

As for other aspects seen in the IPCE spectra for different deposition thicknesses, a myriad of careful considerations of different factors has to be taken into account. The percentage of IPCE fluctuations can be traced back to the cavity size (diameter) of the sample, which matches the peak resonance wavelength. More important than the IPCE itself is the ratio of the photocurrent peaks. This ratio (extracted from Figure 5.13 through Figure 5.15) documented in Table 5.2, reflects the plasmonic enhancement at different deposition thicknesses and temperatures: the higher the Vis/UV ratio, the higher the plasmon resonance. For 0.5*D*, the highest ratio is observed at 450°C and 550°C. The wide cavity opening at this deposition height (~ 600 nm) allows the maximum exposure of the Au substrate to visible irradiation, resulting in a local peak resonance at wavelength ~ 590 nm without diminishing the UV peak.

Deposition Height	Vis/UV ratio		
	450°C	550°C	650°C
0.4 <i>D</i>	0.118	0.147	0.197
0.5 <i>D</i>	0.146	0.189	0.159
0.6 <i>D</i>	0.111	0.119	0.161
0.7 <i>D</i>	0.107	0.149	0.284
0.8 <i>D</i>	0.111	0.126	0.141
0.9 <i>D</i>	0.123	0.169	0.147

Table 5.2 Comparison of the Vis/UV peak ratio for different annealing temperatures

The fluctuating ratios of other thicknesses and temperatures can be traced back to the compensating effects between the diameter to peak resonance and the Au abundance, where a structure of 0.9*D* may present a poorly resonating structure but a large Au surface for electron storage. The oscillation frequency upon irradiation can generate different cross sections for optical processes including scattering and absorption. This is dependent on one condition: the Au structure size should be larger than 50 nm, below which no resonance is expected since the mean free path of electrons in Au lies in that range⁹⁸. The LSPR of arbitrary shapes and sizes of Au have attracted lately major interest, and can be calculated thoroughly within the Discrete Dipole Approximation methods (DDA).

5.3.2 Photocurrents and IPCE ($D = 500$ nm)

As for the previous samples throughout this work, where it commenced with depositing polystyrene spheres of $D = 600$ nm, the same is done with $D = 500$ nm spheres, proceeding similarly with the Au deposition, followed by TiO_2 deposition and annealing. Measurements were focused on the 500 nm sphere samples annealed at 550°C since, as already mentioned above, maximum photocurrent yields are observed due to an optimal crystallinity induced at this temperature, as well as the enhanced interfacial contact between Au and TiO_2 , also known as grafting.

Figure 5.16 Photocurrent measurements (left) for TiO_2/SSV ($D = 500$ nm) samples annealed at 550°C and the corresponding IPCE (right)

As noticed in Figure 5.16, similarly evaluated from the corresponding photocurrent curve on the left, changing the sphere diameter further affects the IPCE shape: the UV absorption edge is shifted slightly to wavelengths > 400 nm for deposition heights $> 0.4D$. This is accompanied by a significant increase of the IPCE in the visible range, resonating once again with the reduced spherical void diameter, reaching remarkable values up to almost 4% and broadened absorption compared to literature⁸¹.

5.3.3 Supplementary LED illumination

In order to further investigate the plasmonic effects, a Light Emitting Diode (LED) source was superimposed in the optical path to the xenon lamp irradiation. The amber LED of few mW power, emits at 590 nm wavelength, matching the peak in the visible range for samples with $D = 600$ nm voids. In the wavelength-dependent spectra for a $0.4D/550^\circ\text{C}$ sample (*cf.* Figure 5.17), a mere increase of 100 nA.cm^{-2} in the photocurrent upon LED irradiation, complementary to the monochromatized white light, is accompanied by a significant $3\text{ }\mu\text{A.cm}^{-2}$ increase in the resonant TiO_2 band transition. This observation highlights the plasmon-induced enhancement, and shows that an additional irradiation can give rise to new plasmonically excited electron-hole pairs, by a mechanism involving the injection of hot electrons in the conduction band of TiO_2 . This subsequently results in higher photocurrents with the assistance of plasmon-induced resonance energy transfer (PIRET), which allows the energy absorbed in the plasmon resonance to be transferred to TiO_2 ⁹⁹.

Figure 5.17 The effect of superimposed LED irradiation upon TiO_2/SSV substrates on wavelength-dependent photocurrents

5.3.4 Band gap determination

The optical property of Au, that its LSPR lies between 530 and 620 nm, arises as a result of the collective modes of oscillation of the free conduction band electrons induced by interaction with the electromagnetic field⁹⁵. The shift of the resonance frequency values depends on the concrete geometry of the resonant cavities. The aforementioned property implies that it is possible to tune the photo-absorption by control of the sphere diameter¹⁰⁰ (*cf.* Figure 5.18). A similar phenomenon has been observed by Wang et al.¹⁰¹ where they study how the absorption peak in TiO₂ tunes with the LSPR of Au nanoparticles with which TiO₂ is doped.

Figure 5.18 Comparison of photocurrent spectra for two different cavity diameters of the SSV substrates (left) and Fowler plots for band gap determination (right)

Reducing the spherical cavity diameter is also reflected in a band gap reduction of the system from 3.09 eV for $D = 600$ nm voids in comparison to 3.2 eV for bulk anatase TiO₂ and a significant decrease to 2.65 eV for $D = 500$ nm voids, which supports the broadened absorption peak for the latter.

All the arguments concerning charge transfer and plasmon-induced enhancement effects presented above, help put together a diagram (*cf.* Figure 5.19) which can simplify the clarification of phenomena occurring upon irradiating the photoanode at different wavelengths. Under UV light, *i.e.* for $\lambda < 400$ nm (3.1 eV), electron-hole pairs are generated in the semiconductor (TiO₂), at an

increased rate in presence of the Au SSV substrate due to the enhanced electric field which could be attributed to a mechanism similar to that depicted in Figure 3.2 (b). This regime is characterized by large photocurrents, where the holes in the VB participate in the oxygen evolution reaction. The Au surface not only acts as an electron sink, trapping electrons to hinder their recombination, but also acts as a mirror increasing the path length for incoming photons¹⁰², where photons not absorbed in the semiconductor upon their first pass could be reflected at the semiconductor/Au interface to be reabsorbed upon a second pass. Additionally, the bare Au surface plays an essential role as a catalyst for hydrogen evolution.

Figure 5.19 Proposed rationalization of the photocatalytic activity of the TiO₂/Au-SSV under UV irradiation (left), and upon excitation of the Au surface plasmon under visible irradiation (right) – inspired by^{103,104}

Upon visible irradiation, *i.e.* for $\lambda > 500$ nm (2.48 eV), the roles of metal and semiconductor switch, since at a suitable wavelength corresponding to LSPR conduction in Au, the metal absorbs photons and performs a plasmon-mediated charge injection of an electron in the semiconductor CB which could be attributed to a mechanism similar to that depicted in Figure 3.2 (a). A spectroscopic transition, which normally takes place in the UV, can in this case be excited by visible light³⁵. The electron has sufficient energy to cross the space charge layer^{105,106}, resulting in a significant photocurrent^{107,108}. The hole remaining in the metal close to the Fermi level assists the mechanistically complex oxidation reactions at the Au surface, with the reduction reactions possibly driven unconventionally at the semiconductor¹⁰⁹.

5.3.5 Recombination times determination under solar irradiation

The Solar Simulator modulated photocurrent measurements have been carried out using the setup described in Section 4.6 for all samples of $D = 600$ nm voids annealed at 450°C, 550°C and 650°C at all Au deposition heights, as well as those of $D = 500$ nm annealed at 550°C. The photocurrent generated upon irradiation with an AM 1.5 source, which is the difference between illuminated and dark current, was compared to the Vis/UV ratios from Sections 5.3.1 and 5.3.2., and summarized in Figure 5.20. The trends are very similar between the two quantities, with both being largest at deposition heights ranging between $0.5D$ to $0.7D$, which further supports the role of plasmonic resonance in inducing photocurrent yields upon illumination in the visible range as the solar simulator's spectrum begins at ~ 370 nm (*cf.* Figure 4.7)

Figure 5.20 Overview of modulated photocurrent plots compared to Vis/UV ratios of PEC measurements for $D = 600$ nm (left) $D = 500$ nm/550°C (right). The data have been acquired under AM 1.5 irradiation with means of a solar simulator

The charge recombination process due to plasmonic effects and the photocurrent-transient measurements described in the previous section provide a quantitative tool to calculate electron-hole recombination times. Exemplary photocurrent-transient measurements for $0.3D$ and $0.5D$ are shown in Figure 5.21. Let $D = \frac{I_t - I_{st}}{I_{in} - I_{st}}$, where I_t , I_{st} and I_{in} are the time-dependent, steady state and initial photocurrents respectively^{99,110} highlighted in Figure 5.22 for the same samples as above.

Figure 5.21 Transient current measurements for 0.3D (left) and 0.5D (right) under AM 1.5 irradiation with means of a Solar Simulator.

Figure 5.22 Anodic transient currents under AM 1.5 irradiation with means of a Solar Simulator for sample 0.3D (left) and 0.5D (right) showing the initial and steady state currents

It may be seen that the quantity D , which is a scaled and normalized photocurrent, has an exponential decay in time. The time constant of this decay is related (or equal) to the electron-hole pair lifetime. The recombination times are then defined as the values where the curves in Figure 5.23 intersect with the grey dotted line at $\ln(D) = -1$. The values $\tau_{0.3D} = 0.246$ s and $\tau_{0.5D} = 4.551$ s are obtained for systems 0.3D and 0.5D. Electron-hole recombination is virtually suppressed for 0.5D as obtained by previous reports¹¹¹, observed qualitatively with the slower decay behavior in comparison with 0.3D, due to the plasmonic trapping effects. The SSV structure acts as a sink for electrons to prolong the carrier lifetimes, made possible by the intense localized electromagnetic field gradient present in the patterned Au SSV.

Figure 5.23 Normalized plots of $\ln D$ vs. t for recombination times estimation

5.3.6 UV-Vis characterization of reflectance and absorbance

UV-Vis spectrophotometers allow researchers to gain broad knowledge about optical (reflectance and absorption) properties of samples. These data reflect more or less directly the electron structure of the system and are comparatively easy to acquire. To analyze the $\text{TiO}_2/\text{Au-SSV}$ samples, a UV-Vis spectrophotometer of model UV-2600 Integrating Sphere (Shimadzu), with dual beam and two sources (deuterium and tungsten) was used in reflectance mode. The bare SSV (without TiO_2) was first used as a reference sample to set the reflectance threshold and then samples with two void diameters ($0.6D$ for $D = 500/600$ nm) were measured. An example of the reflectance spectrum is given in Figure 5.24 (left) and its transformation to an absorbance spectrum using the Kubelka-Munk method^{112–115}. In Figure 5.24 (right), a complex resonance peak structure is observed in the 300 - 700 nm range. The absorption peak in the visible range resonates with the sphere diameter, with the presence of the UV peak at 300 nm noticeable. The additional peak at around 450 nm could be due to interference effects in the thin film sample geometry. The Kubelka-Munk approximation is rigorously valid for negligible background reflection and infinitely thick samples. The latter were performed in air in the spectrophotometer, as opposed to the photocurrent measurements in the electrochemical cell in 0.1 M NaOH electrolyte.

Figure 5.24 Measured diffuse reflectance spectrum and transformed absorption (Kubelka-Munk) spectrum (left) comparative absorbance spectra for two samples with void diameters 500 nm and 600 nm (right)

5.4 Raman Analysis

5.4.1 Dependence on annealing temperature and deposition height

A detailed and concrete Raman analysis was done on all TiO_2/SSV samples using the setup described in Section 4.8. An exemplary spectrum is given below (*cf.* Figure 5.25), showing all characteristic peaks of anatase^{116,117}. A 97% anatase content is confirmed according to the Renishaw built in library of WiRe 4.1 software used for this analysis, with the bands summarized in Table 5.3. A typical dual peak of the 513 cm^{-1} and 519 cm^{-1} bands is usually present at low temperatures (73K). Only the peak at 519 cm^{-1} is present in the spectrum taken at room temperature, summing up to a total of five peaks for anatase, seen for all samples annealed at 450°C and 550°C .

Figure 5.25 Raman spectrum for TiO₂/Au-SSV (550°C) taken with N PLAN EPI 50×/0.75 objective

In samples annealed at 650°C (*cf.* Figure 5.26), the appearance of two extra peaks at 447 cm⁻¹ and 612 cm⁻¹ indicates a slight percentage of rutile ¹¹⁸. All previous anatase peaks remaining unchanged, except for the peak at 639 cm⁻¹ which merges into a small shoulder of the peak at 612 cm⁻¹. The quantification yields an 83% anatase and 11% rutile content, with the rutile bands ¹¹⁹ summarized in Table 5.3. The band at 447 cm⁻¹ is related to oxygen atom liberation and the small shoulder at ~243 cm⁻¹ could be attributed to a two-phonon (second order) Raman scattering ¹²⁰. The sharp peak at 144 cm⁻¹ corresponds to the anatase phase, and overlaps with the weak band at 143 cm⁻¹ for rutile ¹²¹. This specific sharp peak will be the focus of the next section, where its intensity will help understand the dependence of the TiO₂ film structure on annealing temperature as well as the underlying deposition height of the Au SSV.

Figure 5.26 Raman spectrum for TiO₂/Au-SSV (650°C) taken with N PLAN EPI 50×/0.75 objective

Band (cm ⁻¹)	Symmetry	Mode	Strength	Assignment
			<i>w: weak, m: medium, s: strong, vs: very strong</i>	
143	B _{1g}	O-Ti-O bending	<i>w</i>	rutile
144	E _g	Ti-O stretching	<i>vs</i>	anatase
197	E _g	Ti-O stretching	<i>w</i>	anatase
399	B _{1g}	Ti-O stretching	<i>m</i>	anatase
447	E _g	O liberation	<i>s</i>	rutile
513	A _{1g}	O-Ti-O bending	<i>m</i>	anatase
519	B _{1g}	O-Ti-O bending	<i>m</i>	anatase
612	A _{1g}	Ti-O stretching	<i>s</i>	rutile
639	E _g	O-Ti-O bending	<i>m</i>	anatase
826	B _{2g}		<i>w</i>	rutile

Table 5.3 Overview of Raman modes for anatase and rutile TiO₂

5.4.1.1 $\lambda = 633$ nm for $D_1 = 600$ nm and $D_2 = 500$ nm

The SERS intensity is closely related to the substrates' optical properties, *i.e.* reflection or absorbance, which is strongly influenced by the geometry. This makes the SERS intensity highly dependent on the cavity diameter and height and the resulting plasmonic modes^{55,62,85}. The annealing temperature also influences the intensity of Raman bands, typically increasing with temperature as the crystallinity improves^{122–125}. All the aforementioned aspects are summarized in the bar chart below (*cf.* Figure 5.27) showing the Raman intensity dependence of the 144 cm⁻¹ anatase band on annealing temperature and cavity height for two sphere diameters under 633 nm irradiation. Under same measuring conditions (laser power and exposure time), spectra corresponding to $D = 600$ nm show much larger intensities due to the improved resonance between the void diameter and the incoming laser wavelength. Other than a clear increase with increasing annealing temperatures, heights between $0.5D$ and $0.7D$ seem to have the most active plasmonic modes, resulting in substantial enhancement.

Figure 5.27 Bar graphs showing the intensity of the very strong E_g band for anatase at 144 cm^{-1} as a function of annealing temperature and Au-SSV deposition height for $\lambda = 633$ nm, with sphere diameters $D = 600$ nm (left) and $D = 500$ nm (right)

5.4.1.2 $\lambda = 532$ nm for $D_1 = 600$ nm and $D_2 = 500$ nm

Upon changing the laser irradiation wavelength to $\lambda = 532$ nm, a quite similar resonance phenomenon seems to dominate SERS intensities. Not only does the temperature trend influence the intensity substantially (*cf.* Figure 5.28), but again the deposition heights between $0.5D$ and $0.7D$ seem to also have the highest Raman intensity, alongside resonance between the sphere diameter and the laser wavelength. Those of $D = 500$ nm reveal larger intensities in absolute number of counts.

Figure 5.28 Bar graphs showing the intensity of the very strong E_g band for anatase at 144 cm^{-1} as a function of annealing temperature and Au-SSV deposition height for $\lambda = 532$ nm, with sphere diameters $D = 600$ nm (left) and $D = 500$ nm (right)

5.4.1.3 Theoretical comparison

For the $D = 600$ nm system, a copolarized absorption study has been presented by Baumberg et al. for TM and TE polarizations at a zero azimuthal orientation. TM (Transverse Magnetic) is p -polarized light, as in linearly polarized with direction lying in or *parallel* to the plane of incidence. Similarly, TE (Transverse Electric) is s -polarized light, as in polarized perpendicularly (german: *senkrecht*) to the plane of incidence. The two laser wavelengths have been added as a guide to the eye. Different thickness regimes could be identified based on the dispersion maps, where at heights ranging from $0.08D$ to $0.4D$ Bragg modes are seen, as expected, with the latter disappearing at heights ranging from $0.4D$ to $0.9D$, as the surface breaks up into islands. Mie plasmons then appear and they can be recognized by being almost independent of incidence angle, as they are confined (trapped) modes as mentioned before in Section 3.3. At heights $0.9D$ to $1.14D$, the void is encapsulated and the Bragg modes reappear. Strongest are the modes between $0.5D$ and $0.7D$ which agrees quite well with our Raman results showing a correlation of the intensity to the deposition height and consequently existing plasmon modes.

This also supports the corresponding high ratios of Table 5.2 for the photocurrent measurements as it partly reflects the plasmon strength and resonance. The plasmon modes are medium-dependent in the sense that they not only behave slightly differently in different media with respect to their dispersion, but the overall Raman intensity is influenced, as mentioned in Section 3.2, by the medium's index of refraction n . The drop in intensity is proportional to n^4 , e.g. a factor of 2.8561 is expected for water, of $n = 1.3$ ⁴⁹. The samples have been measured in 0.1 M NaOH using the self-designed cell described in Section 4.8 coupled with the long-distance objective, and the anatase peaks seem to drop by a factor of ~ 4 which is in good agreement (not shown here as the vibration bands do not change). The additional drop could be due to experimental drawbacks such as the electrolyte meniscus, that being slightly denser than water, as well as light scattering and losses along the optical path as the long-distance objective requires a working distance of 8 mm in contrast to 0.5 mm for measuring in air.

Figure 5.29 Dispersion maps for increasing void thicknesses from $0.08D$ to $1.14D$ on a Au SSV array with $D = 600$ nm, for photon energies from 0.7 eV to 2.5 eV. Logarithmic color scale from black (maximum reflectivity) to white (minimum reflectivity)⁵¹

5.4.2 Potential-dependent SAM peaks using EC-SERS

Another application for sculpted Raman active substrates is in electrochemical investigation of adsorbed molecules such as self-assembled monolayers (SAMs) on the surface. Potential-dependent SERS peaks could elucidate reaction pathways that are not clear from cyclic voltammetry alone. The orientation of adsorbed molecules, such as SAMs, is potential-dependent as shown by Chao et al.¹²⁶ who examined mercaptopyrindine layers adsorbed on a roughened silver electrode and found that the molecule lies almost parallel to the surface at low potentials and almost perpendicular to it at more positive potentials. The interaction between the charged electrode and the molecule allows the latter to be either attracted to the surface, increasing the Raman signal as it approaches, or repelled into the bulk electrode, decreasing the signal intensity as the molecule is now further away from the surface. Mercaptoundecanol (MUO) was used here as a test molecule adsorbed on the SSV, with an exemplary spectrum shown in Figure 5.30, measured on a 500 nm void SSV template with a laser wavelength of 532 nm to improve resonance effects.

Figure 5.30 Raman spectrum for 0.5D SSV ($D = 500$ nm) modified with MUO at $\lambda = 532$ nm, taken with HC PL FLUOTAR L50 $\times$ /0.55 long-distance objective in 0.1 M NaOH (left) chemical formula of MUO ¹²⁷ (right)

Five bands are present in the spectrum and could be assigned as follows: 780 cm^{-1} (C–S stretching), 1040 cm^{-1} (C–O stretching), 1066 cm^{-1} (C–H bending), 1556 cm^{-1} (C–C stretching) and 1640 cm^{-1} (O–H bending) ¹²⁸. The complete series of potential-dependent spectra measured in the stability range of the SAM (0 to 500 mV vs. SCE (*cf.* Figure A.5)) is shown in Figure 5.31 (top left). Information gathered about the peak intensity and position is summarized in the adjacent plots for every peak, where the shift in peak position hints at an electron density change in the molecule upon interaction with the substrate. Surprisingly only peaks at 780 cm^{-1} (C–S stretching) and 1556 cm^{-1} (C–C stretching) show a decreasing intensity with increasing potential from 0 to 500 mV, probably since the C–S and C–C bonds are nearest to the surface as the SAM anchors its sulfur to Au.

Figure 5.31

Summary of the Raman spectra of MUO adsorbed on the SSV structure under potential control (top left) with intensity and position plots for all characteristic MUO peaks under $\lambda = 532 \text{ nm}$, taken with HC PL FLUOTAR L50x/0.55 long-distance objective

5.5 BiVO₄ as a Photoanode

Another promising candidate for photoelectrochemical water splitting purposes is the well-studied ^{129–131} environmental-friendly bismuth vanadate BiVO₄. It presents the advantage of low cost, non-toxicity and convenient production techniques. BiVO₄ will be eventually deposited on the TiO₂/Au-SSV substrates to form a hybrid photoanode characterized in Section 5.5.5. With a relatively low band gap of 2.4 eV ¹³², BiVO₄ compensates for its high electron-hole recombination rates, which have been investigated in the present work by doping with Ag, which similarly to Au, has an LSPR enabling strong absorption in the visible spectrum region.

In this section, electrochemically deposited BiVO₄ films on FTO substrates are analyzed, which were produced under various pH and temperature conditions. Subsequently, Ag nanoparticles were deposited electrolessly on etched silicon wafers after testing several parameters, such as dipping durations and solution concentrations. Samples have been further characterized electrochemically using CV and wavelength-dependent chronoamperometry. The structure of the BiVO₄ film and the size and shape of the Ag particles have been acquired via AFM, SEM and Raman Spectroscopy, using techniques and experimental setups which have been described in Chapter 4.

5.5.1 Deposition and its conditions

The FTO coated glass substrates were thoroughly cleaned with deionized water and dried in a nitrogen stream. For the electrochemical deposition of BiVO₄ films, a metal salt solution was freshly prepared by mixing 10 mM Bi(NO₃)₃ and 35 mM VOSO₄, acidified by adding nitric acid to a pH value little below 0.5. With the help of a 2 M sodium acetate solution, the pH was raised to around 5.1 and then lowered back to the required pH of 4.7 by further adding nitric acid. Here the acetate is crucial to stabilize the Bi(III) ions, which are insoluble at pH 4.7 ¹³³. Different pH values between 3.9 and 4.7 were tested for the deposition process,

with the result that at pH 4.3 the most homogeneous films could be achieved as seen under the microscope. For the actual electrochemical deposition, a standard three-electrode cell was used, with the FTO substrate as the working electrode, a Platinum wire as counter electrode and a standard calomel electrode (SCE) serving as reference. A deposition potential of 1.9 V was applied for various durations after several preliminary tests were made with increasing increments of 0.1 V up to 2.2 V. Afterwards, the substrate was rinsed with deionized water, dried in a nitrogen stream, and ramp-annealed at 500°C to avoid eventual temperature-induced defects in the deposited film. Finally, the substrates were immersed in a 1M KOH solution for 10 minutes in an ultrasonic bath to eliminate the newly formed vanadium oxide surface layer.

5.5.2 Doping of BiVO₄ films with Ag under UV irradiation

Two methods were used for growing Ag particles on the BiVO₄ films from an AgNO₃ solution treated with 1M KOH. Both electroless dipping techniques were performed for three different times (10, 20 and 30 minutes) to investigate the particle growth rate as a function of time, once as a dark dipping technique and alternatively while irradiating the deposition beaker with a UV lamp at 365 nm wavelength. The UV light irradiation should generate an excess of electrons in the CB, which help reduce silver ions in solution, accelerating the nanoparticle deposition.

First attempts at electroless Ag deposition were done on etched *n*-type silicon wafers, with the aim of transferring the acquired knowledge to the *n*-type BiVO₄ films. Dipping the wafers for a few minutes in a 1 mM AgNO₃ solution showed the formation of a quite homogeneous distribution of Ag nanoparticles. These are of around 40 nm in size by careful AFM analysis, which is smaller than the critical diameter of 50 nm, necessary for sustaining plasmonic modes in Ag¹⁰⁰. A ten-fold increase in the AgNO₃ solution concentration, however, had a more drastic influence on the size of the Ag nanoparticles than a longer dipping time, leading to an increase in the particle size to larger than 110 nm. As a consequence, the resonant photon scattering would increase, which is ruled out for Ag nanoparticles below the critical diameter of 50 nm. Further Ag deposition on the

BiVO₄ films was done from a 10 mM AgNO₃ solution exclusively. “Dark” dipping for 10 minutes in the AgNO₃ solution revealed the growth of micrometer-long rod-like particles dispersed on the surface of BiVO₄ films, where EDX confirmed the rods to be of pure Ag. However, doubling the dipping time showed a completely different Ag deposition, where very fine Ag grains cover the BiVO₄ film completely. Finally, tripling the dipping time to 30 minutes seems to induce an agglomeration effect on the aforementioned grains, forming Ag clusters where the latter exhibit highest photocurrents in the wavelength-dependent measurements.

Interestingly, in the UV-assisted Ag deposition, the Ag particles formed after 10 minute deposition time turned out to be micron size spherical ones, and almost homogeneously distributed across the surface. Further increasing the deposition time showed an increase in the number of particles formed on the surface, with their shape and size remaining unaltered. This is in contrast to the “dark” dipping, where qualitatively different phenomena have been observed at each of the three deposition times. Under UV illumination, an external polarization of the working electrode is needed to modulate a selective and patterned metal deposition on n-type semiconductors. The photogenerated electrons activate the deposition, as they possess sufficient energy to reach the oxide layer conduction band, even under electroless conditions^{134,135}. Desorption induced by electronic transition (DIET) processes could be attributed to this result, if the metal particles in the deposition solution are isolated. The SEM image (*cf.* Figure 5.32) shows the BiVO₄ substrate after 30 minutes deposition under UV irradiation. The spherical Ag particles are clearly recognized on the surface, where the EDX spectra 1 and 2 of the particles exhibit a large extra Ag peak.

Figure 5.32 SEM image of a BiVO₄ substrate obtained after 30 minute Ag deposition under UV irradiation (left) EDX spectra on selected spots of the deposited film (right). Deposition time for the BiVO₄ film in the electrochemical cell was 3 hours.

5.5.3 Raman characterization

Raman measurements have been performed on all substrates after the electrochemical deposition to make sure that the films were exclusively of BiVO₄ nature. Figure 5.33 (black curve) shows a Raman spectrum of a bare BiVO₄ sample after a three hour electrochemical deposition under 633 nm irradiation, revealing all characteristic peaks¹³⁶ at 210 cm⁻¹, 324 cm⁻¹, 366 cm⁻¹, 640 cm⁻¹, 710 cm⁻¹ and 826 cm⁻¹.

Figure 5.33 Comparative Raman spectra showing the characteristic BiVO₄ peaks for the bare substrate and the Ag-doped ones, following dipping for the indicated time under UV irradiation, $\lambda = 633$ nm, exposure time: 10 seconds, taken with N PLAN EPI 50 $\times$ /0.75 objective

Simultaneously, all samples have been inspected with the integrated optical microscope at different magnifications of 50× and 150× to examine film homogeneity as a function of deposition time. Lower deposition times (30 minutes – 1 hour) lead to uncovered FTO areas, designated as “gaps”. The latter have been adequately covered after deposition longer than 2 hours. Films formed after 3 and 4 hours show the most homogeneous structure and non-existing gaps. As a good compromise between deposition time and film homogeneity for the Ag deposition studies, a standard deposition time of 3 hours has been selected.

Figure 5.33 summarizes, compared to the bare substrate, the spectra of the BiVO₄ films modified in three Ag-doping time intervals designated as Ag(UV). Clearly, the enhancement increases for the Ag-doped films, due the metal's LSPR nature and its impact on the surface-enhanced substrate. The generated electromagnetic field at the nanoparticle couples preferentially to the mode at 826 cm⁻¹ that is enhanced systematically as the Ag-doping time increases. The enhancement of Raman modes correlates to the particle density and its dispersion on the non-resonating BiVO₄ surface^{137,138}.

5.5.4 Photoelectrochemical characterization of Ag-doped BiVO₄ films

A similar enhancement phenomenon is observed for the wavelength-dependent photocurrent spectra of Ag-doped BiVO₄ films, where an almost ten-fold increase is seen (with the Ag modification) at the peak around 465 nm (*cf.* Figure 5.34). The Ag particles induce renounced light scattering, enhancing the absorption in BiVO₄ due to surface plasmonic effects, which channel energy from the electromagnetic wave through the metal to the semiconductor. Electron-hole pair recombination is hindered by the electric field generated upon illumination. The field propagates from the metal particle at the surface and triggers charge carrier separation, assisting the water oxidation¹³⁹. The peak is of relatively comparable intensity for all Ag-modified samples, however, one should note that a 30 minute modification results in a photocurrent increase at all irradiation frequencies larger than the band gap compared to bare BiVO₄. The absorption over the spectral range 300 – 515 nm increases systematically with Ag dipping time, dropping back to zero at 515 nm (2.4 eV) which corresponds to the semiconductor's band gap.

Figure 5.34 Photocurrent spectra of a bare BiVO₄ and BiVO₄/Ag(UV) substrates; in 0.1 M NaOH (aq). Deposition time for the BiVO₄ film in the electrochemical cell was 3 hours.

The cyclic voltammogram shown in Figure 5.35 depicts the first cycle of all Ag-doped substrates at three different times of UV irradiation, in comparison to the reference substrate without Ag modification. A trend is visible with increasing deposition time: not only does the current increase considerably with increasing deposition time, but a simultaneous shift in the onset potential is observed in both oxidation and reduction regions. The current increase observed with increasing Ag modification time as well as the potential shift indicate that the particles play a beneficial role as co-catalysts in the water oxidation once they surpass a critical size and abundance.

Figure 5.35 First cycle of several BiVO₄ substrates after various Ag(UV) deposition. All potentials are indicated vs. SCE, in 0.1 M NaOH (aq), scan rate 10 mV.s⁻¹

5.5.5 Hybrid BiVO₄/TiO₂/Au-SSV structure

The BiVO₄ deposition process described in Section 5.5.1 was repeated on TiO₂/Au-SSV structures with the aim of forming a hybrid structure. The presence of a substrate different than FTO accelerated the BiVO₄ deposition, complete coverage occurring after less than 2 minutes. Figure 5.36 shows the images after 30 and 60 seconds deposition time, where the surface is readily almost completely covered. For a 30 second deposition time resulting in few BiVO₄ particles, the photocurrent black curve shows a small peak between the UV and visible peak of the TiO₂/SSV structure which could be attributed to the BiVO₄ absorption at around 465 nm (as seen in Figure 5.34). The green curve, corresponding to a 60 second deposition shows a drastic increase in the visible light absorption in the entire 300 – 600 nm range while compromising the UV peak, as most of the TiO₂ is now covered by BiVO₄ as observed in the AFM image (inset), with the plasmonic contribution still discernible in the small shoulder at around 600 nm.

Figure 5.36 Wavelength-dependent photocurrent spectra for the hybrid structure of BiVO₄/TiO₂/Au-SSV after 30 and 60 seconds deposition time with the corresponding color-coded AFM images.

The dependence of different BiVO₄ film deposition processes on solution pH, applied potential, deposition time and annealing temperature has been investigated with the aim of parameter optimization. For deposition under UV illumination (at 365 nm), the reduction as well the homogenous deposition of catalytically active Ag particles has been facilitated. The deposited Ag particles showed increasing Raman enhancement with increasing UV-induced deposition time. The impact on the CV results was highlighted with manifold currents increasing almost linearly with particle abundance and redox potential shifts. Wavelength-dependent photocurrent effects have been observed, with increasing photocurrent peaks at around 465 nm and broad absorption shoulders in the UV range. In summary, a relatively simple, reproducible, and non-toxic method with abundant precursors has been presented for manufacturing a composite plasmonically active semiconductor. This promising method is certainly of relevance to improve sustainable and environmental friendly solar energy conversion.

6 Conclusion and Outlook

Optimal harvesting of the natural solar spectrum for water splitting applications has led to adapting inadequate wide band gap semiconductors. Traditionally, this procedure has been widely explored in the past decades, mostly by depositing nano-sized noble metal co-catalyst particles onto massive semiconducting photoanodes for facilitating the sluggish oxygen evolution reaction, requiring four electrons, and being the bottleneck of water photoelectrolysis. In the conventional design of optimized band gap photoanodes, the catalytic properties of the deposited nanoparticles have played a major role. Electro-catalytically active metals which are also transition metals, are well known for their advanced plasmonic and optical properties, as spectacularly manifested in effects such as those observed by shining light through a cathedral's stained glass, or into the Lycurgus cup. A systematic exploitation of synergies between the plasmonic activity of the noble metal co-catalyst and the semiconductor component of the photoanode is of wide and renewed interest. The present work may be seen as a further contribution in this recent research direction. Moving away from the traditional design principles, the metallic component of the present photoanode is an extended (Au) film, nanostructured by a regular array of spherical voids, with dimensions comparable to the wavelengths in the visible spectrum (500 – 600 nm). The semiconductor component (TiO_2) is deposited onto this underlying gold support possessing a refined nano-antennae structure, closely mirroring the periodicity of the support. In the ideal case, the semiconducting layer would form a system of identical, regularly placed pillars, separated by voids in the substrate, exposing clean spherical segment voids (SSV). The rationale behind this engineered structure is the possibility of enhanced performance by injecting the plasmonic activity of the Au-substrate into the semiconducting subsystem by close proximity effects. An example of this synergistic effect is the resonant transfer of plasmonically excited electrons from the metal into the conduction

band of the semiconductor via so-called PIRET processes¹⁴⁰. In summary, with the present design we have reached a satisfying compromise solution between several conflicting demands typical of solar-harvesting photoanodes. Two major problematic trade-offs were elegantly resolved in the system studied in the scope of this work. The first, quite elementary one, is high chemical stability in the dark and under illumination that increases generally with increasing band gaps, such as that of TiO₂, thus reducing the overall efficiency. The Au support and the pillared, cost-effective and stable semiconductor structure of reduced band gap, solve the problem at hand in the effort of enhancing wide band gap systems. A complementary trade-off is that of catalysis and recombination, where the noble metal centers set to originally serve catalytically become efficient recombination centers. Tuning the void size to match the metal's localized surface plasmon resonance (LSPR) allows it to absorb photons more efficiently, overcoming the problem in the attempt of ultimately succeeding in PEC water splitting.

We have observed an enhanced photoabsorption in the UV range on the patterned nanostructure configuration, which due to presence of Au voids supports the dual role of the latter, being a sink for electron trapping and suppressed recombination, as well as a mirror, increasing the path length of incoming photons. The absorption peaks of the visible domain seen in the photocurrent measurements, and subsequently their corresponding IPCEs, show a clear resonance between the void diameter and the incoming irradiation wavelength. This is clearly attributed to tuning the system's LSPR via its geometry to the incoming irradiation, as also seen in the Raman measurements. The highest Raman intensity for a characteristic anatase TiO₂ band is observed for 500 nm voids whilst irradiating with a laser of wavelength 532 nm, and for 600 nm voids with one of 633 nm. The aforementioned observations in the visible range of the light spectrum reveal the crucial role of the underlying Au substrate which absorbs photons and carries out a mediated electron injection in the TiO₂ pillars to induce photocurrent generation in energies below the semiconductor's band gap. Modulated measurements under AM 1.5 conditions, which replicate the natural irradiation of a complete solar spectrum, provide a quantitative tool for calculating charge carrier recombination times, clearly hindered in the presence of Au voids.

As an extension, we investigate the fabrication of a different semiconductor component, BiVO_4 deposited electrochemically on FTO, throughout this work as well as its modification with Ag nanoparticles in a UV-mediated electroless dipping procedure. Combining this middle band gap metal oxide to the $\text{TiO}_2/\text{Au-SSV}$ system, as a hybrid photoanode extension, showed interesting growth and photoabsorption properties. Enhanced interfacial charge transfer kinetics of metal oxide/noble metal composites and hybrids thereof have potential applications for better understanding and improving the performance of PEC solar cells. The light has been also shed on plasmonic hot-spot photocatalysis in recent studies where the influence of nanostructuring the metal, as in this work, has been highlighted as Au nanostars endowed TiO_2 with a stronger catalytic enhancement compared to still the classic case of Au nanospheres or Au nanorods^{141,142}.

Several systematic and experimental modifications could be applied to the present combination in order to harvest higher photoabsorption and increase efficiencies. A new PEC cell design, which is in progress, is a very important factor in increasing the IPCE numbers. Losses resulting from inefficient cell geometry due to reflection losses from window surfaces, absorption by the window, electrolyte or metal contact, and finally reflection instead of absorption from the photoanode are issues to be optimized in the new cell. Integrating gas chromatography or pressure gauges to quantify the corresponding products of water splitting is an inevitable tool in further characterizing the system. Also interesting would be gathering information on plasmonic absorptions and their variations as a function of void diameter and film thickness. This could be analyzed via normal incidence or angle resolved reflectance spectra upon shining white light on the sample, and collecting the reflected light over a very small aperture using an automated goniometer. The dispersive properties of noble metal SSV systems with different sizes and periodicities can be quite intriguing, especially after depositing the metal oxide on its rims. The latter of a different index of refraction could affect the optical properties to be measured concretely with the goniometer and better explain the photoelectrochemical results. This tailored morphology and the wide range of novel applications it offers can be very beneficial in employing classical materials for clean and renewable technologies.

Appendix

A.1 Cyclic Voltammetry

A.1.1 Substrate characterization of different Au nature

It has been previously mentioned that the nature of physical vapor deposition (PVD) coated Au thin films and that deposited electrochemically are different. To further understand their similarities and differences, CVs of well known Au surfaces such as the single crystal (111) and polycrystalline Au (pc) have been carried out to study a way to better match the Au slide and Au SSV. The results are summarized in Figure A.1.

Figure A.1 Comparative CVs for four different Au substrates in 0.1 M H₂SO₄ (aq). All potentials are indicated vs. SCE, scan rate 10 mV.s⁻¹ (Courtesy of Heiko Müller, Institute of Electrochemistry, Ulm University)

The CV for Au (111) is depicted as the typical “swordfish” form which is characteristic for this electrode in sulfuric acid. Starting from a potential which is negative of the point of zero charge (-0.2 V vs. SCE) to preserve the thermally reconstructed herringbone surface¹⁴³ and avoid specific adsorption of anions, the scan domain extends positively to 0.9 V and back to -0.3 V. At around 0.3 V a large peak is seen, which denotes the lifting of the reconstruction caused by the start of specific adsorption of hydrogen sulfate and the reduction of the surface charge on the electrode. This is accompanied by the growth of monoatomic-high Au islands on the Au (111) surface as it was relatively compressed by the reconstruction.

Increasing the potential further induces the sharp spike seen at around 0.8 V that reflects a phase transition and rearrangement within the layer of surface adsorbed hydrogen sulfate, stabilized by the co-adsorption of hydronium. The complementary spike in the cathodic scan is the lifting of the hydrogen sulfate ordering, followed by the potential-induced reconstruction at around 0.2 V which is less pronounced as in the anodic scan, as the layer is now less densely packed and less ordered.

Compared to the well-ordered Au (111) single crystal, the polycrystalline Au wire has a totally different CV, as the wire has all the predominant crystal facets. The early hydrogen evolution at around -0.3 V could be due to foreign metal impurities such as Pt, and the small shoulder at around 0.35 V correlates to OH⁻ adsorption. At the SSV surface, the hydrogen sulfate adsorption peak is around 0.5 V, and both oxidation and reduction peaks are shifted due to blocking effects caused by solutions with which the substrates have been last treated such as DMF or the commercial brightener. One could say that it is the slide that shares most similar features with Au(111), be it in regard to current densities, or the general voltammogram shape, and therefore it is referred to as a *pseudo*-111 surface.

However, what all these substrates have in common is their high stability, corrosion resistance, chemical inertness, and the strong Au/S interaction, which makes it possible to build stable and ordered SAM structures with sulfur end groups due to this high affinity^{144,145}.

A.1.2 Unit cell approximation and comparative CVs

Considering the SSV geometry, and the dimensions and pattern given by the SEM image below, a unit cell approximation was set up to analyze the discrepancies in the CVs with and without TiO_2 . The cell is defined as a 6×6 cavities template that are hexagonally packed of $D = 600$ nm and inter-cavity distance of 100 nm, confirmed by the SEM image for $0.5D$ in Figure A.2 (left). This will result in area $A = 4.942 \mu\text{m}^2$ and $B = 20.357 \mu\text{m}^2$, hence losing area A after TiO_2 deposition, which is 20% of the total area ($A+B$) and the approximate percentage in current decrease between the red and blue curves (*cf.* Figure A.3).

Figure A.2 Unit cell approximation for a 6×6 unit cell for $D = 600$ nm spheres at $0.5D$ height

Figure A.3 Comparative CV's for bare SSV (black) modified with SAM (red) with TiO_2 deposited on top (blue) for $0.5D$, $D = 600$ nm, in 0.1 M NaOH (aq). All potentials are indicated vs. Ag/AgCl, scan rate 5 mV.s^{-1}

A.1.3 Potential cycling under intermittent illumination

Cyclic Voltammetry (CV) measurements have shown that the photocurrents generated in the wavelength-dependent curves can be mirrored via modulated (chopped) cycling at the peak wavelengths. For a 0.8D/550°C sample, CVs were carried out in the dark as well as chopped under illumination at the peak wavelengths of $\lambda_1 = 320$ nm and $\lambda_2 = 590$ nm (*cf.* Figure A.4). Using the setup described in Section 4.5, the monochromator was set to $\lambda_1 = 320$ nm and chopped for 10 seconds between illuminated and dark conditions at a potential scan rate of 5 mV.s^{-1} . The same was done for $\lambda_2 = 590$ nm. Interestingly, the currents chopped at the given wavelengths have the same ratios like those in the wavelength-dependence (Vis/UV ratio of 0.126), confirming yet again the LSPR role. The values of unilluminated chopped currents overlap nicely with the CV in dark (black curve), where the peak at around 100 mV is associated with reversible OH^- desorption^{146–148}.

Figure A.4 Dark and light-chopped (10 second period at $\lambda_1 = 320$ nm and $\lambda_2 = 590$ nm) CV measurements for the 0.8D sample of $D = 600$ nm, annealed at 550°C , in 0.1 M NaOH (aq). All potentials are indicated vs. Ag/AgCl, scan rate 5 mV.s^{-1}

Figure A.5 CV used for potential-dependent Raman measurements in Section 5.4.2, showing in grey bullets the Raman measurement potentials in the forward scan, and in blue bullets those in the backward scan. The cell is the self-designed Raman cell, which has no possibility of purging, hence the slight tilt in the CV taken in 0.1 M NaOH (aq). All potentials are indicated vs. SCE, scan rate 10 mV.s^{-1}

A.2 SHINERS Approach to SERS and its Transfer to SSV Substrates

A practical application of SERS involving coinage metals is using shell-isolated nanoparticle enhanced Raman spectroscopy (SHINERS) that replace the need for roughening the surface itself and could therefore allow any substrate or morphology, even single crystals to be used as an active surface in SERS studies. It harnesses the enhancing properties of nanoparticles like Au, that are covered in an ultrathin chemically passivating silica shell, such that the Raman signal increases while avoiding a chemical influence of the SHIN's on the studied surface reactions¹⁴⁹. This is achieved by the so-called “borrowed” SERS effect, as the stable thin shell enables the transfer of long-range electromagnetic fields, but still ensures no contact between the substrate under study and the underlying Au nanoparticle, imitating a tip placed in close proximity to the surface, as in Tip-Enhanced Raman Spectroscopy¹⁵⁰.

This approach was adapted to deposit a thin layer of SiO_2 on the Au SSV substrates and to study its behavior in possibly enhancing the LSPR peak. The effects could be by broadening the LSPR peak or eventually red-shifting it, for applications in dye degradation or photoreduction¹⁵¹.

The method used was a standard sodium silicate reduction method. As a linking primer, (3-aminopropyl)trimethoxysilane (APTMS) is crucial to anchor the Au surface to the silica coating, where one monolayer is adsorbed to the Au driven by the large complexation of amine groups, which is sufficient for homogenous coating^{152,153}. The SSVs were modified for 15 minutes with a 1 mM solution of APTMS, in parallel to a bare Au slide as control sample. The next step was introducing the sodium silicate solution for shell formation, where the standard thickness ranges between 1 nm and 5 nm when the pH of the solution is between 10 and 11. Since a much thicker layer is desired, and to increase the deposition rate, the pH was reduced to 8.6 by adding hydrochloric acid to the sodium silicate solution. The samples were immersed in the latter and left to rest at room temperature for about 10 minutes for the first silicate layer to form, then placed on a heating plate at 90°C and stirred occasionally for 1 hour to accelerate the process. Slides and SSVs were then cleaned thoroughly with deionized water, dried in a nitrogen stream and stored until transferred to the SEM chamber.

Figure A.6 SEM image showing a SiO₂ cluster on the Au slide (control sample) with corresponding color-coded EDX on and outside of the cluster

Figure A.6 shows an SiO_2 cluster on the Au slide, confirmed by EDX. Contrary to what is formed on the SSV: a rectangular block is seen in Figure A.7, which suggests that the deposition, even though resulting in a 27% Si weight in both samples, is quite local, uneven and behaves very differently on the two surfaces.

Figure A.7 SEM image showing a deposited SiO_2 rectangular block on the Au SSV, with corresponding color-coded EDX on and outside of the block area

In the attempt to homogenize the deposition, the linking primer was replaced with (3-mercaptopropyl)triethoxysilane (MPTS) with sulfur as an end group, which possibly anchors better to Au. The modification was done with a 20 mM MPTS solution for 1 hour and the samples then immersed in a 10 mM NaOH solution for 2 hours, to cross-link the MPTS monolayer primer¹⁵⁴. The rest of the process, involving sodium silicate immersion, heating, stirring and cleaning, was identical to the one described earlier involving APTMS. After careful SEM analysis, no traces of SiO_2 were found. Improvement of deposition parameters such as temperature, solution concentrations, or possibly longer modification times with either APTMS or MPTS might lead to stronger linker anchoring and eventually to a homogeneous deposition.

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Symbols and Abbreviations

AFM	Atomic Force Microscopy
AL	Accumulation Layer
APCE	Absorbed Photon-to-current Conversion Efficiency
CB	Conduction Band
CBD	Chemical Bath Deposition
CE	Chemical Enhancement
CT	Charge Transfer
CV	Cyclic Voltammogram
DL	Depletion Layer
DMF	Dimethylformamide
EDX	Energy Dispersive Xray
EE	Electromagnetic Enhancement
EF	Enhancement Factor
EM	Electromagnetic
EU	European Union
FTO	Fluorine doped Tin Oxide
FVB	False Valence Band
HOMO	Highest Occupied Molecular Orbital
IPCE	Incident Photon-to-current Conversion Efficiency
IR	Infrared
LED	Light Emitting Diode

LSPR	Localized Surface Plasmon Resonance
LUMO	Lowest Unoccupied Molecular Orbital
MFON	Metal Film Over Nanosphere
MONERS	Metal Oxide Nanoparticle Enhanced Raman Scattering
MONP	Metal Oxide Nanoparticle
MUO	Mercaptoundecanol
NHE	Normal Hydrogen Electrode
NIR	Near Infrared
NP	Nanoparticle
OCP	Open Circuit Potential
ORC	Oxidation and Reduction Cycling
PEC	Photoelectrochemical
PIRET	Plasmon Induced Resonance Energy Transfer
PS	Polystyrene Spheres
SAM	Self Assembling Monolayer
SCL	Space Charge Layer
SEM	Scanning Electron Microscope
SERS	Surface Enhanced Raman Spectroscopy
SPP	Surface Plasmon Polariton
SSV	Sphere Segment Void
STH	Solar To Hydrogen
TE	Transverse Electric
TM	Transverse Magnetic
UV	Ultra Violet
VB	Valence Band
VIS	Visible

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Article	Influence of grain boundaries on elasticity and thermal conductivity of nanocrystalline diamond films, M. Mohr, L. Daccache, S. Horvat, K. Brühne and T. Jacob, H.J. Fecht, <i>Acta Materialia</i> 122 (2017) 92-98
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Article	Electrochemical SERS: In-depth investigation of electrocatalytic formic acid oxidation on modified Au surfaces, H. Müller, J.M. Hermann, L. Daccache, C. Adler, M. Metzler, L.A. Kibler, T. Jacob - in preparation
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