A Dye-sensitised Schottky Junction Device fabricated from Nanomaterials on a Stainless Steel Substrate

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Dye-sensitised Schottky junction cells were fabricated on stainless steel using TiO$_2$ and silver nanowires. A titania sol was synthesised by a sol-gel process and was deposited on the substrate by dip coating, followed by sintering at 350°C for grade 304 stainless steel. Silver nanowires were drop cast from suspension and annealed. The current-voltage characteristics were measured and fit to the diode equation. The average I$_0$ value for a typical batch of anatase devices was 4.9×10^{-6} A cm^{-2}. The devices showed a UV response after treatment with tartaric acid and showed EQEs of 7.0 % in the UV at single wavelengths. It was possible to measure a small visible photocurrent for these devices following functionalisation with a ruthenium dye.

Introduction

Photovoltaic and photocatalytic cells with high efficiency, low cost, high stability and made from abundant materials provide a formidable fabrication challenge. There are a range of architectures of third generation solar cells which aim to reduce the need for the low defect single crystal films typically used in first generation silicon solar cells. [1] Whilst most commercial photovoltaic cells are manufactured from crystalline silicon, many promising second and third generation devices are emerging, with good efficiencies reported for thin film chalcogenides, perovskites, organic and dye-sensitised solar cells (DSSCs). [2] The sensitization of Schottky barriers to produce a photocurrent has also been demonstrated, though with low reported efficiencies. [3]

An example of a dye-sensitised Schottky barrier device was formed following the sensitization of a thin gold film on TiO$_2$ with merbromin dye. [3] The proposed mechanism for the transport of electrons from the dye was by ballistic transport through the gold film. [3]

A similar architecture can also be used to produce Schottky barrier cells from p-type materials namely PbSe nanocrystals, which showed an impressive efficiency of 2.1 % under AM 1.5G, but with limited stability in air. [4] Further, a Schottky barrier device was formed between a TiO$_2$ film functionalised with an inorganic dye and a thermally evaporated gold contact. [5] The dye functionalisation resulted in altered diode characteristics, with rectification increased by several orders of magnitude and showing a limited photoresponse, all achieved with the Ru(dcbpy)$_2$(NCS)$_2$ (where dcbpy is (2,2'-bipyridine)-4,4'dicarboxylic acid) dye. [5]

As has been widely studied on a variety of substrates, Schottky barrier height is impacted by surface states and DFT studies of TiO$_2$ appear to corroborate this for TiO$_2$/noble metal systems. Schottky barrier height has been studied using a DFT model of a TiO$_2$ and Au interface and this suggests the Schottky barrier can decrease from 0.87 eV to 0.15 eV when there are oxygen defects present on the TiO$_2$ surface. [6]

A Schottky barrier can be formed between nanoparticulate silver and gold on the semiconductor in DSSCs to improve the charge collection at the semiconductor/solvent interface. The Schottky barrier increases the residency time of electrons in the semiconductor, as observed by measuring the dynamics of recombination of a fluorescent dye on ZnO nanorods modified by Au nanoparticles. [7] There is also evidence to suggest a Schottky barrier formed between compact TiO_2 and an Indium Tin Oxide (ITO) substrate in a DSSC can cause current loss, by reducing the current collection rate at the back electrode of a DSSC. [6]

This work focussed on the fabrication of Schottky junctions that can be made under standard laboratory conditions utilising dip coating and drop casting. The devices can be fabricated on stainless steel with a titania sol, with a top contact of silver nanowires from a suspension. These devices can then be functionalised with dyes and a small visible photocurrent can be measured. Electrons from the excited dye molecule can transfer from the dye excited states to the TiO_2 conduction bands for collection at the substrate. Electrons are proposed to transfer from the silver nanowires to the dye, as illustrated in Figure 1 to repopulate the dye ground state. Under illumination of the device under UV light, the device will function as a conventional Schottky junction cell (Figure 1)

[Figure 1]

Figure 1: Illustration of the mode of action of a dye-sensitized Schottky barrier device formed between silver nanowires and a semiconductor (not to scale).

In the examples of such devices found in the literature, noble metals have been thermally evaporated onto substrates under vacuum, or deposited electrochemically. [3][5] However, due to the use of dispersed silver nanowires, several different areas used in this work must be defined and are illustrated in Figure 2. The geometric area is defined as the physical area of the device being equal to the area of the steel substrate. The shadow area is defined as the coverage of the silver nanowires, as measured from a typical SEM image. The junction area is defined as the area available for functionalisation is that around the nanowires and depends on the lateral extent of the Schottky barrier.

[Figure 2]

Figure 2: Demonstrating the different defined areas of the device.

Experimental procedure

In a typical TiO_2 sol synthesis, 12 ml of isopropyl alcohol, 1 ml of deionised water and 1 ml nitric acid (70 %) are stirred vigorously. 0.5 ml of titanium isopropoxide (97 %) was added dropwise and stirred for > 30 mins yielding a pale yellow transparent viscous liquid. For an anatase sol, this liquid is hydrolysed for 8 hours under reflux. Following this, ammonia solution (30%) was added dropwise with stirring until it is above pH 7 yielding a viscous sol. The steel is cut into small (~1cm^2) pieces and rinsed with isopropyl alcohol. Dip coating was

performed by hand, with excess sol removed by capillary action on lab tissue. Typically 2-4 coats were applied and each coat was left to dry at room temperature before the next dip coating. In a typical device the TiO_2 films were then sintered at 350°C for 90 minutes in a furnace. When cool, the devices are drop cast with 5 µL aliquots using a micropipette, totalling 10-25 µL of a 0.25% m/v silver nanowire (AgNWs) suspension in isopropanol (stated nanowire dimensions 60 nm × 10 µm, diluted from 0.5% m/v suspension). The silver nanowires were annealed at 235°C for 20 minutes to reduce junction resistance. To study the functionalisation of the devices with dye, the devices were soaked in a ruthenium dye ($Ru(dcbpy)_2Cl_2$) in ethanol solution provided by J. Weinstein. The current-voltage measurements have been performed using a Gamry Potentiostat between -1 V and 1V, using a 100 Ω resistor in series with the device to limit the current travelling through the device. Photocurrents have been measured using an arc lamp monochromator (Bentham SSM150Xe Programmable light source) controlled with a program written in-house in C by R.Crook and calibrated with a commercial UV enhanced Si photodiode (Si Series 7 OSD5.8-7 Q Centronic Photodiode).Mathematical analysis of the IV measurements was performed with MatLab software. All chemicals were purchased from Sigma Aldrich and used without further purification unless otherwise stated. 304 and 316 stainless steel was purchased from RS components and Fischer Scientific. ITO coated glass was purchased from Sigma Aldrich.

Results and Discussion

Fabrication

Diodes were fabricated on stainless steel by dip coating the substrate in a TiO_2 sol and then depositing and annealing silver nanowires. Two grades of steel were used; 304 and 316 stainless steel (304 SS and 316 SS respectively). These grades differ in their composition and are compared in Table 1.

| Steel grade | Proportion of element / % | | | | |
	Cr	Ni	Mn	Mo	Si
304	17.5-19.0	8.0-11.0	2.00	-	1.00
316	16.0-18.0	10.0-14.0	2.00	2.0-3.0	0.75

Table 1: Comparison of two grades of steel

Steel forms chromia plates when it is heated, this is one of the ways in which steel self-protects against corrosion and these layers depend on the grade of steel used and its preparation method [8]. The chromia films which have slower growth kinetics than iron oxides act as a barrier to the diffusion of cations from the steel. [9]

The temperature at which diodes could be made depended on the grade of steel used. Whilst devices on 304 SS could be formed at 350 °C but not above these temperatures, the same attempts made on 316 SS were unsuccessful. Only devices formed at higher temperatures, or following a pre-treatment stage of heating the steel to high temperature prior to sintering of the TiO_2 films gave diode IV characteristics on 316 SS. Given that the protective films which form on steel prevent the diffusion of cations, the temperature dependence for the formation of Schottky barriers could be due to diffusion of metal ions through the TiO_2 film.

When 316 SS was heat treated and the oxide manually removed prior to sintering of the TiO_2 film, the devices formed were ohmic, compared to rectifying when the layer was left intact. The diffusion of ions could cause a short circuiting of the Schottky barrier, by formation of ohmic contacts at the interface with the silver nanowires.

Metal diffusion through titania from the substrate has been reported in the literature, for instance, a 90 nm TiO_2 film on 304 SS had 7 mol % Fe content following annealing at 400 °C for 1 hour, and this was detected at the surface of the film in the form of rhombohedral Fe_2O_3. [10] Similarly, the impact of metal diffusion through TiO_2 films for DSSCs has also been studied. Sn diffusion through TiO_2 films used in DSSC's has been measured to occur at a rate of 3.2×10^{-5} μm^2 in a doctor bladed TiO_2 film at 450 °C. [11]

EDX measurements (Figure 3) of devices made on 304 SS show high levels of Fe and Cr in regions both where the film is thin (Figure 3).

[Figure 3]

Figure 3: Top row, left: SEM image of 316 heated steel showing chromia plates. Top row, right: SEM image of thin TiO_2 coating on 304 type steel. Middle and bottom: EDX images of top right SEM image; (centre left) O Kα1, (centre right) Ti Kα1, (bottom left) Cr Kα1 and (bottom right) Fe Kα1.

Current-Voltage Characteristics

Device IV curves were measured with a potentiostat and modelled using a modified ideal diode equation and thermionic emission theory, described by the following equations.

$$I = I_0 \left(\left(\exp \frac{qV}{nkT} \right) - 1 \right) + \frac{V}{R_s} \tag{1}$$

Where I = device current
q = elementary charge
n = diode ideality factor

V = device voltage
R_s = shunt resistance
k = Boltzmann constant
T = absolute temperature
I_0 = reverse saturation current

$$I_0 = SA^*T^2\left(\exp\frac{-\Phi_S}{kT}\right) \tag{2}$$

Where S = junction area
A* = modified Richardson constant
Φ_s = Schottky barrier height

The shunt resistance incorporates electron transport through the device by other mechanisms.

Typical measurements of current and voltage (IV measurements) between room temperature and 100 °C can be seen in Figure 4 for a device of ~1 cm^2.

[Figure 4]

Figure 4: IV curves at a range of temperatures for a typical diode.

To estimate the series resistance, differential resistance was measured between 0.95 and 1.0 V. The outcome of fitting was generally good, 1406 measurements of 487 devices gave R^2 values above 0.99. A set of control devices, made from anatase (24 devices) and amorphous (10 devices) sols of TiO$_2$ and are shown in Table 2. Results for ohmic devices or those with lower R^2 values were discarded.

Control devices	Average I_0 / A	R_{shunt} / Ω	R_{series} / Ω
Amorphous	3.7×10^{-5}	7.2×10^3	1260
Anatase	4.9×10^{-6}	4.2×10^5	190

Table 2: Showing I_0 values for a single series of control devices

Diode properties and temperature

The IV curves of some devices were measured at a range of temperatures. It was found that the I_0 values increased exponentially with temperature up to 100 °C, followed by a linear

decrease. This is possibly due to competition from other competing mechanisms at higher temperatures, in particular, there is likely to be an interface between the TiO_2 layer and a p-type chromia layer on the steel or due to a changing TiO_2 interface with silver. For this reason, in the thermal analysis, only results below 100˚C were used. The error inherent in this method include the problem of temperature fluctuations during the measurements, for which reason, many of the analyses showed poor correlation of I_0 with temperature. Fitting using Equation 2 gave Richardson plots (Figure 5), allowing the estimation of Schottky barrier height (Table 3).

[Figure 5]

Figure 5: Example Richardson plot of reverse saturation current against temperature.

	SBH (thermionic emission theory) / eV	R^2
1	0.91	0.98
2	0.56	0.91
3	1.27	0.94

Table 3: Values from Richardson plots for a range of devices.

The calculated Schottky barrier heights from a range of devices correlated well with the R^2 of the fit of the Richardson plot ($R^2 > 0.8$). The best estimation of the barrier height, at 0 K, is ~0.91 eV, due to its high R^2 value.

Junction area estimates

Although the Richardson plots could be used to deduce the active area of the device, the logarithmic nature of the plots compounded error and resulted in drastically different estimated areas from devices of similar area. The vacuum level of the Richardson constant is 120 A cm^{-2} K^{-2} but this is corrected for the effective masses of electrons in a material being different to that in a vacuum. [12] The best fit, that of Figure 5, gives an area of 0.087 cm^2, using a reported Richardson constant of 24 A cm^{-2} K^{-2} for TiO_2. [12]

A typical device had 59 µg of silver nanowires deposited and assuming they have a density similar to that of bulk silver and their dimensions are as stated by the supplier, on average 10 µm in length and 60 nm diameter, this gives an estimated 3×10^9 wires per device. This is consistent with counting the silver nanowires over a small area of 6.25 µm^2 by SEM and extrapolation to the full area of the device (Figure 6).

This equals an effective surface area of the silver nanowires of ~3.6 cm^2 per device, using their stated dimensions. Comparing to the Richardson plot estimate of 0.087 cm^2, this equates to 2.4% of the wire area. This suggests a low proportion of the silver nanowires are in contact with TiO_2 and are contributing to the junction area of the Schottky barrier. However, some of these will be necessary to forming a conductive mesh on the device, so bringing disparate junction areas into contact and to reduce series resistance.

[Figure 6]

Figure 6: SEM images of a typical silver nanowire device, a 6.25 µm^2 section was analysed to estimate the area covered by silver nanowires by extrapolation.

A report of a 17 mA/cm^2 current flowing through a low resistivity 12 Ω/sq. silver nanomesh has been shown to fail due to heating, with a calculated current density of 4×10^4 A/cm^2 occurring in the nanowires, providing an estimate for failure of the nanowires due to current density. [13] This is higher than the densities calculated for even the smallest junction area estimates in this work.

Photocurrent

Photocurrents under UV light were seen for rectifying devices, however they were very small. Surface states can provide recombination sites, and additives to passivate surface states have been used to give higher efficiencies in DSSCs. [14] For this reason, a range of adsorbents were used in an attempt to improve the UV response of these devices. It was found that tartaric acid was a particularly effective additive.

It was also found that the films typical for the amorphous devices showed little evidence of crystallinity apart from peaks attributable to austenite iron oxides that are the same in the heat treated steel substrate. Typical literature methods for the production of anatase TiO$_2$ sols rely on a prolonged heating step, at an elevated temperature. For this reason, a method was used to produce a more crystalline sol. New sols underwent an 8 hour reflux step, resulting in films that showed very broad peaks that correspond to the anatase phase. The peaks are significantly broader than commercial TiO2 P25 nanopowder, suggesting small crystallite size or defects. This is likely in these samples due to the diffusion of metals from the substrate and imperfect crystallisation. The partially anatase films show a considerable photoresponse in the UV region compared to the amorphous devices (Figures 7 and 8).

Literature DFT studies on amorphous TiO2 have found that the energy for formation of the oxygen vacancy in TiO2 is much lower than in crystalline forms, resulting in relatively good hole transport and that the trapping of holes also occurs more easily. [15] Hole trapping may be a significant loss mechanism in the amorphous devices given the n-type nature of conduction in TiO$_2$.

Both amorphous and anatase devices, with tartaric acid showed higher photocurrents when illuminated with UV light, as shown in Figures 7 and 8.

[Figure 7]

Figure 7: UV responses for an amorphous TiO$_2$ device.

[Figure 8]

Figure 8: UV responses for an anatase TiO$_2$ device.

Current densities of several hundred nA cm^{-2} and up to 1.3 uA cm^{-2} was seen in the UV region, corresponding to 7.0 % EQE at a single wavelength. A series of passivated devices, showing a range of UV responses are shown in Figure 9.

[Figure 9]

Figure 9: UV response for a range of devices, showing a photocurrent density of several hundred nA cm^{-2}.

Modification

Ruthenium dyes containing acid bipyridines show excellent absorption coefficients, allow binding to TiO$_2$ and were used in the first DSSCs. [16] Previous similar work on functionalisation of a TiO$_2$ Schottky barrier device found it was possible to measure a photocurrent following the functionalisation of a TiO$_2$ Schottky barrier with a ruthenium dye. [5]

As such, devices were soaked in Ru(dcbpy)$_2$Cl$_2$, where dcbpy is 2,2'-bipyridine-4,4'dicarboxylic acid, to sensitize the devices. Ru(dcbpy)$_2$Cl$_2$ sensitised devices gave lower I$_0$ values and higher maximum currents on average than the control devices. Some preliminary work shows that this phenomenon is not unique to Ru(dcbpy)$_2$Cl$_2$, with Co(bpy)$_3^{2+}$ NO$_3^{2-}$ (where bpy is 2,2' bipyridine) and organic acids showing improvements to the IV characteristics of the device, suggesting this is not limited to asymmetric ruthenium dyes.

It is possible to achieve a visible photocurrent using a device functionalised with Ru(dcbpy)$_2$Cl$_2$ dye, as shown in Figure 10. The unfunctionalised device shows no photocurrent in the visible region.

These visible responses were uncommon on the amorphous and unpassivated films. Anatase devices functionalised with Ru(dcbpy)$_2$Cl$_2$ and passivated with tartaric acid, and showed a limited photocurrent, dwarfed by the UV response.

[Figure 10]

Figure 10: Photocurrent response from a range of devices functionalised with Ru(dcbpy)$_2$Cl$_2$ showing some limited and varied photocurrent in the visible region.

The measured photocurrents are extremely small, for reference a commercial silicon photodiode provides a maximum of 31.3 µA /cm^2 at ~500 nm under similar conditions. There is also marked variation between the devices which is likely to be due to the variation in active areas for the devices.

For the best device, a peak external quantum efficiency of 6.7×10^{-3} % is found at 520 nm. However, this demonstrates that this architecture functions and that charge separation has occurred at the interface.

Of the whole area of the device, only the junction area is likely to be optically active and therefore the efficiencies will be higher considering just this area, compared to the geometric area of the device of 1cm^2. Table 4 shows adjusted efficiencies. The shadow area is taken to be 0.13 cm^2 and is an estimate for the coverage of the silver nanowires. The best estimate from the thermionic emission analysis, 0.087 cm^2, is used for junction area. The generated current under visible and UV light are due to differing mechanisms, but in both cases, the extent of the area of the junction is going to be important to the measurement of EQE.

It is likely that the overall efficiencies of the devices can be further improved by optimisation of the geometry of the device. For instance, by functionalising the whole area of the nanowires, an area 3 times larger than that of the geometric area would increase the available junction area and the photocurrents could be improved drastically.

Device type	λ / nm	EQE (by GE) / %	EQE (by SA) / %	EQE (by JA) / %
Amorphous	300	0.016	0.12	1.8
Anatase	300	7.0	53.8	80.5
Ru(dcbpy)$_2$ Cl$_2$ sensitised device	520	0.0067	0.052	0.8

Table 4: External Quantum efficiency (EQE) has been calculated as a proportion of the geometric area (GE), taken to be 1 cm^2 and shadow area, taken to be 0.13 cm^2 and the best estimate of junction area, taken to be 0.087 cm^2.

Further improvements could be made by better passivation and fabrication strategies, particularly in the control of crystallisation of TiO$_2$. Also, dyes can be altered continuously and optimised loadings of dyes, co-adsorbents and an improved architecture could all improve efficiency.

Conclusion

A Schottky barrier can be formed over a large area between silver nanowires and TiO$_2$, on a stainless steel substrate. A range of methods have been used but the best results are obtained for 304 stainless steel dip coated in a titania sol which had undergone a reflux step for 8 hours, followed by sintering at 350 ˚C for 90 minutes followed by drop cast silver nanowires. There is no doubt that this process could be improved by further improvements to the sol and to the substrate, particularly to improve the crystallinity of the films used. This is a cheap process requiring no specialist equipment, which may allow the large scale synthesis and

improvement of these systems and their application. The reverse saturation currents could doubtless be improved by small molecule mediation and diode characteristics are altered by acids. Some cells functionalised with a ruthenium dye show a small photocurrent response to visible light, which whilst not at the moment being large enough to be of any practical value, demonstrates the potential use of these cells, as well as showing potential to give information about how a dye and TiO_2 interact in these systems. The sensitivity of these devices to temperature, pH and UV light could also lead to their use as sensors.

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A Dye sensitised Schottky Junction Device fabricated from Nanomaterials on a Stainless Steel Substrate (Figures)
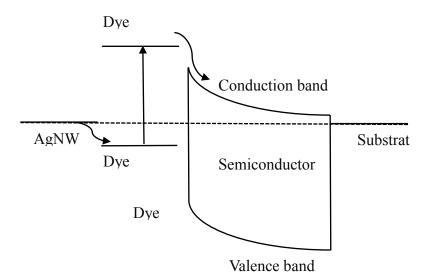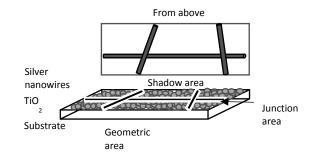

Figure 1: Illustration of the mode of action of a dye sensitized Schottky barrier device formed between silver nanowires and a semiconductor (not to scale).
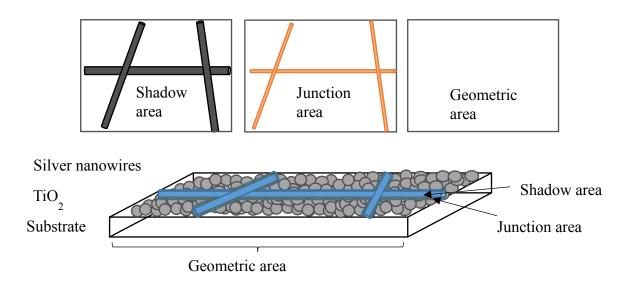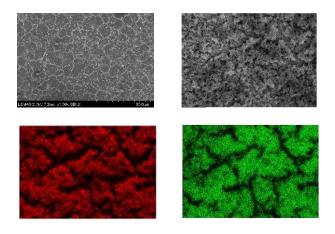
Figure 2: Demonstrating the different defined areas of the device.

	Proportion of element / %				
Steel grade	Cr	Ni	Mn	Mo	Si
304	17.5-19.0	8.0-11.0	2.00	-	1.00
316	16.0-18.0	10.0-14.0	2.00	2.0-3.0	0.75

Table 1: Comparison of two grades of steel

Figure 3: Top row, left: SEM image of 316 heated steel showing chromia plates. Top row, right: SEM image of thin TiO$_2$ coating on 304 type steel. Middle and bottom: EDX images of *top right SEM image; (centre left) O Kα1, (centre right) Ti Kα1, (bottom left) Cr Kα1 and (bottom right) Fe Kα1.*

Equation 1: $I = I_0 \left(\left(\exp\frac{qV}{nkT} \right) - 1 \right) + \frac{V}{R_s}$

Where I = device current

q = elementary charge

n = diode ideality factor

V = device voltage

R$_s$= shunt resistance

k = Boltzmann constant

T = absolute temperature

I$_0$ = reverse saturation current

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Where S = junction area

A* = modified Richardson constant
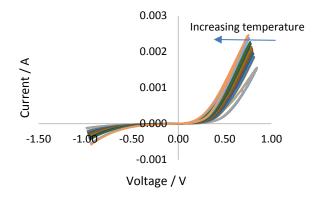
Φ$_s$ = Schottky barrier height

Figure 4: IV curves at a range of temperatures for a diodic device.

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Anatase	4.9×10^{-6}	4.2×10^5	190

Table 2: Showing I_0 values for a single series of control devices

$$y = -10543x + 8.0884$$
$$R^2 = 0.9816$$

Figure 5: Example Richardson plot of reverse saturation current against temperature.

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2	0.56	0.91
3	1.27	0.94

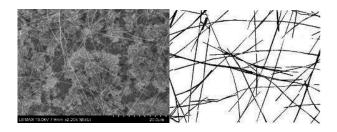Table 3: Values from Richardson plots for a range of devices.

Figure 6: SEM images of a typical silver nanowire device, a section was analysed to find the area covered by silver nanowires.
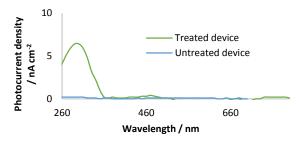

Figure 7: UV responses for an amorphous TiO_2 device.
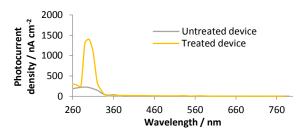

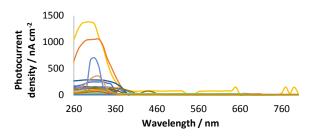Figure 8: UV responses for an anatase TiO_2 device.

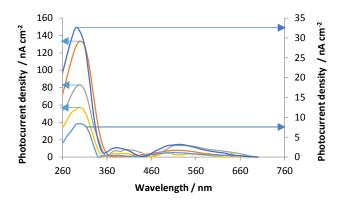Figure 9: UV response for a range of devices, showing a photocurrent density of several hundred nA cm^{-2}.

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Table 4: Efficiency has been calculated as a proportion of the geometric area, shadow area and junction area.