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*Abstract*—We present a novel way to utilize high-concentration photovoltaic (HCPV) radiative losses and diffuse light, otherwise unused in conventional HCPV systems, to power an Imperial College designed photoelectrochemical reactor (PECR) producing $H_2$ fuel through water splitting. A high efficiency photovoltaic (HEPV) is embedded inside a Luminescent Solar Concentrator (LSC). Edge emission from the radiative recombination loss mechanism in the HEPV is guided within the LSC to the PECR photocathode, whilst the LSC emitted light is guided to the photoanode. The photon streams can be independently optimised in intensity and wavelength. We demonstrate how photon streams with balanced intensity can be achieved.

*Index Terms*—geometrical optics, luminescent devices, photoluminescence, quantum wells, ray tracing, solar cells.

## I. INTRODUCTION

The extraction of hydrogen from water using sunlight was first proposed 30 years ago[1]. Recently interest in the subject is fueled by the need to find a renewable, sustainable and environmentally safe alternative form of energy storage. The main challenge in this field of research is finding a material that can match the energetic and stability requirements of spontaneous photo-water splitting [2], and a breakthrough in this would be the surest way to reach efficiencies high enough to seriously consider commercialisation [3].

The ultimate aim of this project, in conjunction with the Chemical Engineering department at Imperial College London, is to demonstrate photoelectrochemical (PEC) water splitting using photoanodes and photocathodes (Figure 1) that are independently illuminated by two photon streams that are conventionally regarded as waste from HCPV operation. A further advantage of the scheme is that the intensity and wavelength of each photon stream can be independently optimised. The system would produce zero-carbon hydrogen for energy storage and transport as a by-product of HCPV electrical power generation. These two waste photon streams are 1) light that is emitted due to dominant radiative recombination mechanisms at high cell operating bias and 2) entirely unused diffuse light.

We present a concept that merges conventional CPV and LSC technology into a hybrid system that can both generate electricity and generate hydrogen through PEC water splitting.
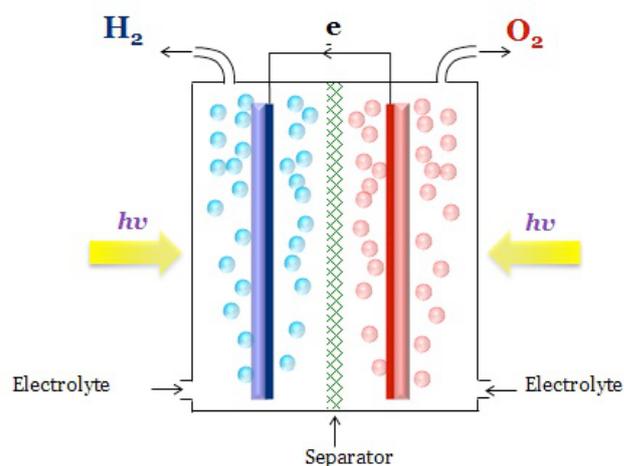


Fig. 1. Schematic of a doubly illuminated photoelectrochemical reactor (PECR). The photoanode (red) produces oxygen molecules through oxidation of water whilst the photocathods (blue) produces hydrogen molecules through the reduction of hydrogen ions.

## II. A SYSTEM OVERVIEW

A diagram of the system is shown in Figure 2. The challenge of directing two separate photon streams to individual photoelectrodes can be solved with a modified luminescent solar concentrator (LSC). The LSC, first introduced in the 1970s, in its basic design is a transparent waveguide structure, either homogeneously doped with, or coated with, luminescent material (luminophores). The luminophores absorb incident light at or above their absorption threshold, and re-emit it with a certain redshift with ideally near unity luminescent quantum yield (LQY). A large fraction of this emitted light is waveguided by total internal reflection (TIR) to the structure's edges, where it is collected by optically coupled optoelectronic devices. The main benefit of using a LSC is the ability to tune its absorption/emission spectra according to different needs, by using different luminophore species. The LSC will provide one of the photon streams by absorbing diffuse light, re-emitting it and waveguiding it into the photoanode of the PECR.

For the other photon stream, we will use high efficiency photovoltaics (HEPV). HCPV modules utilise low-cost optical

elementsto reduce the amount ofsemiconductor needed by concentrating direct sunlight onto these very small but high-efficiencycells.This replacement ofexpensivesemiconductor withcheaper opticsprovides a routetowards reducing the costs of solar electricity generation. A conventional HCPV module consists ofthree elements: Theconcentrating optics, the solar cells and the housing. The aimis to concentrate light as much as possible, onto a HEPV, and to dissipate heat as much as possible.

Any high quality HEPV at high cell operating bias will experience radiatively dominatedrecombinationlosses.There-fore at its maximum power point, when forward biased by theabsorption of concentratedsunlight, a HEPV can act like an edge emitting LED. However, quantum well solar cells (QWSCs) are particularly suitable for this application for three reasons: 1) As will be discussed, their radiative efficiency canbesimply established from measurements of quantum efficiencyand dark current. 2) The radiative recombination takes place at the bottom ofthe quantum well. Quantum wells are acommon feature of LEDsbecause oftheir high radiative efficiency and because the barrier and substrate materialsl is transparent to the radiation. 3) The wavelength and intensity of the emission can beoptimised for agiven catalyst or photoelectrode simply bythe choice of well depth.

The HEPV, which will have antireflection coating on its edges, isembedded in andoptically coupled to, an undoped waveguide whichforms the transparent substrate of a square LSC with thin-film luminescent coating on the topsurface, as in Figure 2.

AFresnel lens concentrates direct light onto aquantum well solar cell (QWSC) to generate aphotocurrent, as per conventional HCPV functioning. Dependingon the QWSC material structure and operating conditions, acertain fraction ofthe light from radiativerecombinationwill bewaveguided to the edges andbe coupled into the LSC, where it gets trapped due to total internal reflection, and waveguided to the photocathode. The majority of the edge emission from the QWSC will be at an angle greater than the escape cone from the top and bottomsurfaces of thewaveguide [4]. The emission willalso be longerwavelength that theluminescence from theLSC coating.Hence the thin-film coating of the LSC will not absorb the radiation from the QWSC.

Inaddition to theessentially isotropicdiffuse contribution of light to the LSC, there is also a contribution from the circumsolar sunlight due to the scattering of sunlight by atmospheric aerosols. The intensity of the short-wavelength photon streamcan thereforebe optimisedfor given spectral conditions by adjusting theacceptance angleof the CPV system.

Wavelength selective mirrors, which are coupled in between the LSC and the photoelectrodes, provide the means to direct the two photonstreams to their desired locations. The photoan-ode, which in our scheme isilluminated by short wavelength light is coupled to thewaveguide through afilterthat transmits light in the visible range, and reflects it in theinfrared range. The photocathode which on our schemeabsorbs infrared light
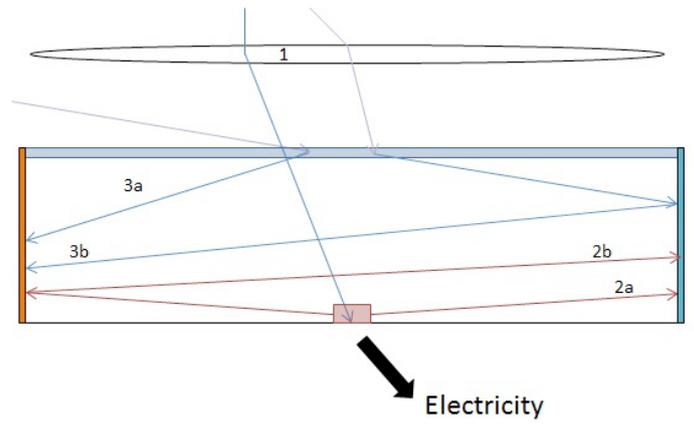


Fig. 2. Summaryof thehybridsystemoptics.1)Directlightisconcentrated onto ahigh efficiency PV cell by Fresnel lens. 2) Emission from radiative recombination escapes from the PV and is waveguided into the reactor photocathode by (a) direct from PV edge, or (b) via hot mirror reflection. 3) Diffuse light is absorbed, re-emitted and waveguided into thereactor photoanode a) directly from luminescent re-emission, or b) via cold mirror reflection.
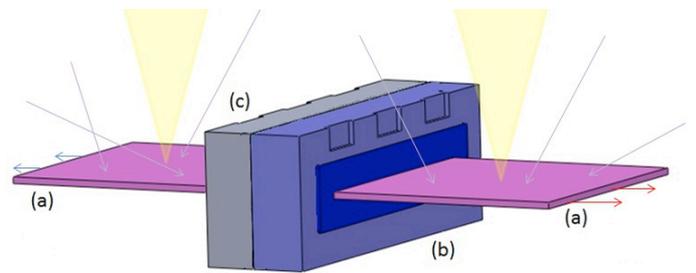


Fig. 3. Overview ofthe hybridsystem, with ahigh efficiency photovoltaic (HEPV) embedded within a luminescent solar concentrator (LSC) (a). Con-centrated direct light enters the solar cell, and UV/blue diffuse light gets absorbedby the LSC. The resultant emitted light from both the LSC and the QWSC gets waveguided into both the photoanode (b) and photocathode (c) sections of the PECR respectively. Note themodularityofthe system, where an array of LSCs/PECRs is possible.

iscoupledtothe waveguide byafilterthat transmits light in theinfraredand reflectsit inthe visible range. The two other edges as well asthe undersideof the LSChave Lambertian high reflectivity air-gap reflectors to minimise escape losses.

Thewavelengthsofthe photonstreamsareengineered to be appropriate for the electrodematerials thus allowingthe water splittinghalf reactions that produceH $_2$ to occurwithin the PECRs. As shown in Figure 3, the system is designed to be modular, with a view of creating a series of arraysof LSCs and PECRs. Figure 4 shows how the reflectivity spectra for the mirrors correspondwell with thespectra for both photon streams.

III. TESTING THE PRINCIPLE OF THE QUANTUMWELL SOLAR CELL ACTING AS LUMINESCENTSOLAR CONCENTRATOR

A. Premise

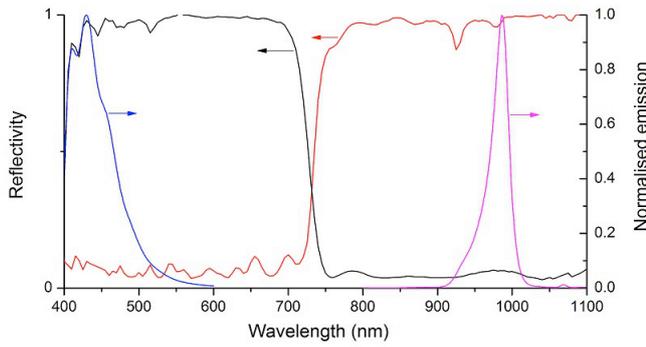The starting point of system optimisation is the initial calculation of the powerdensity that can be achieved bythe

Fig. 4. Reflectivity of the cold (black) and hot (red) mirror as a function of wavelength at 0°angle of incidence. The LSC emitted light (blue) gets transmitted by the hot mirror and reflected by the cold mirror, whereas the opposite happens for the HEPV edge emission (magenta).
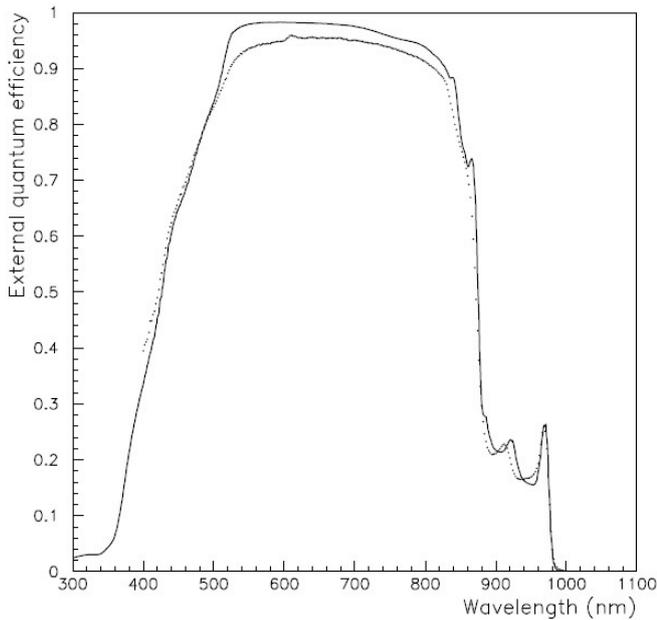


Fig. 5. Measured and fitted external quantum efficiency (EQE) of a p-i-n strain-balanced quantum well solar cell, with its dark current in Figure 6
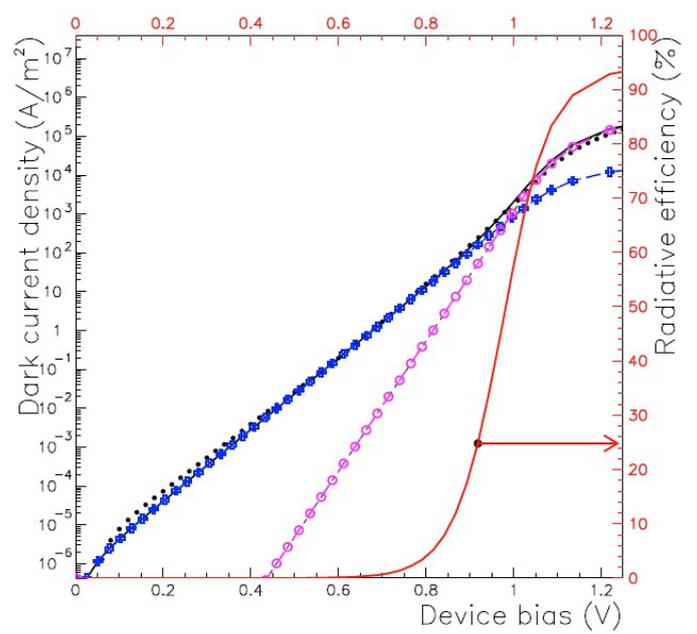


Fig. 6. Measured (black dots) and fitted (black line) dark-IV curve of a p-i-n strain balanced quantum well solar cell. The radiative contribution (magenta) is a prediction based on the quantum well absorption aobratined from the quantum efficiency fit in Figure 5. The SRH contribution (blue) is a one parameter fit

LSC and the HEPV. In this section we present the calculations for both power densities when the system is illuminated under ASTM G-173 conditions [5] and the HEPV is being operated at 500x concentration.

### B. Luminescent Solar Concentrator

For our calculations we use a thin-film luminescent solar concentrator (LSC), with a luminophore/poly(methyl methacrylate) (PMMA) film blade coated onto a UV-transparent glass substrate. The photoanode absorbs light at wavelengths shorter than 500nm. Therefore we utilise Lumogen FViolet 570 (LV570), a naphthalimide-based luminophore. It absorbs light in the 300nm-410nm region, and emits in the 390nm-550nm region with a luminescent quantum yield of around 85%. The optical concentration $C_{opt}$, defined as the ratio of photon flux coupled from the edges to the incident photon flux, can be manipulated by changing the geometry of the LSC. We use a combination of our in-house raytracer PVTrace[6] and the SMARTS sky spectral irradiance calculator[7] to give performance characteristics of the LSC in ASTM G-173 conditions.

The LV570 luminophore is mixed with PMMA at a dye load concentration of 1.5% and given dimensions of 200x 200 x 5mm. With PVTrace we simulated the performance of this LSC setup under incident light conditions of an isotropic hemispherical light source with the spectrum of the diffuse component of ASTM G-173. The calculated optical efficiency of this setup was 2%, giving a photon output of $1.9 \times 10^{17} \text{s}^{-1}$.

### C. Quantum Well Solar Cell

QWSCs, first invented by Barnham and Duggan[8], offer an way to improve multi-junction solar cells by the ability to tune their bandgaps, as well as enhancing photon coupling due to recombination being dominated by radiative processes at high concentration (in excess of 200 suns) [9] -[11].

We demonstrate the principle of a QWSC acting as an LED with a number of square photoluminescence samples of different sizes from a wafer QT1604 grown by MOVPE at the EPSRC National Centre for III-V Technologies at Sheffield. It consists of 22 strain-balanced GaAsP/InGaAs quantum wells in a GaAs p-i-n structure. There was an AlGaAs window below the p-doped GaAs emitter layer that can produce some limited transverse waveguiding due to its comparatively low refractive index. The edges of the photoluminescence sample

were anti-reflection coated.

In order to determine the power density coming out of the edges of the device when illuminated with 500x concentration, we must determine a) its radiative efficiency for a given incident power density and b) its waveguiding capabilities. This is done by a combination of modelling and edge photo-luminescence measurements.

The radiative efficiency of a given QWSC can be determined by fits to the quantum efficiency and dark current as demonstrated in Figure 5 and Figure 6, with a fitting model, SOL [12]. The radiative efficiency is expressed as:

$$\eta_{rad} = \frac{J_{rad}}{J_{rad} + J_{SRH}} \qquad (1)$$

Where $J_{rad}$ is the radiative recombination current contribution and $J_{SRH}$ is the Shockley-Read-Hall non-radiative recombination current contribution. This efficiency is demonstrated in Figure 6 as the red line. The low bias dark current is fitted by Shockley-Read-Hall recombination with one parameter: the effective lifetime for carrier trapping. The radiative contribution to the dark current (magenta circles in Figure 6), which results in photon emission from around the first exciton in Figure 5, is an absolute prediction based on detailed balance assuming photon absorption is given by the fit to the QE around the first exciton feature. This procedure is similar to the determination of the secondary emission from a luminescent species in a LSC.

The merit of using a non-metalised photoluminescence sample is that it functions under open-circuit voltage $V_{OC}$, and without the complication of series resistance that causes the dark-current to curve at high bias in Figure 6. Under $V_{OC}$ conditions, the current $J_V$ in the cell is zero, therefore the short circuit current $J_{SC}$ equals the dark current $J_D$ due to the expression:

$$J_V = J_{SC} - J_D \qquad (2)$$

The short circuit current $J_{SC}$ is expressed as[4]:

$$J_{SC} = q \, \eta \frac{P_{opt}}{h\nu} \qquad (3)$$

where $P_{opt}$ is the incident optical power density and $\eta$ is the quantum efficiency

At open circuit $J_{SC} = J_D$ and from Figure 6 the radiative efficiency and hence the radiative contribution to the dark current density can be determined. The radiative current through the cell is the product of this radiative current density and the sample area. The current is converted into a photon flux by dividing by the electronic charge. The photon flux at the cell edge depends on the cell waveguide efficiency $\eta_C$. The photon flux at the PEC depends on the LSC waveguide efficiency at the wavelength of the emission.

QT1604 was uniformly illuminated with a 532nm beam from a Millennia V laser with two different power settings. A shield blocked all incident and top surface PL light from entering the detector. A calibrated fibre spectrometer was coupled onto an edge of QT1604 to give an absolute spectrum
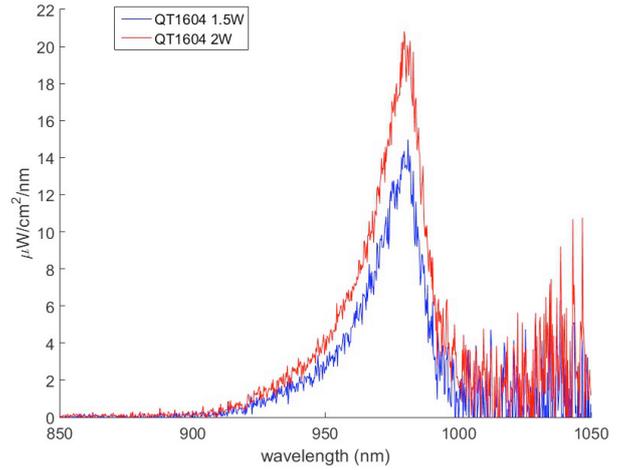


Fig. 7. Spectral irradiance of the edge emission from QT1604, a quantum well solar cell PL sample

in units of $\mu$Wcm$^{-2}$nm$^{-1}$, shown in Figure 7. The curves were fitted to Gaussian functions and integrated to give a value of power density leaving one of the edges. Multiplying up by the area of the edge of the sample we obtain the power out of the edge. To calculate the maximum photon flux coming out of the edges of the sample, we will use Equation 3 with the method mentioned previously.

Using the incident photon flux and the EQE of the sample, we calculate the dark current $J_D$. Using the radiative efficiency $\eta_C$ we obtain a radiative current $J_{rad}$. By dividing by charge $q$ and the area of the edge of the sample we obtain a maximum edge photon flux out of the edge. Multiplying this value by four gives total maximum photon flux out of all edges of the sample.

Having the photon flux from the edge, and all the other parameters for Equation 1 and Equation 2 we can establish the waveguide efficiency of the sample:

TABLE I
MEASURING THE WAVEGUIDE EFFICIENCY OF PHOTOLUMINESENCE SAMPLE QT1604

| | | |
|---|---|---|
| Photon flux incident on top surface (m$^{-2}$s$^{-1}$) | 2.04x10$^{23}$ | 2.74x10$^{23}$ |
| $J_D$ (A/m$^2$) | 3.0x10$^4$ | 4.02x10$^4$ |
| Radiative efficiency | 0.85 | 0.86 |
| $J_{rad}$ (A/m$^2$) | 2.55x10$^4$ | 3.46x10$^4$ |
| $I_{rad}$ (A) | 6.37x10$^{-1}$ | 8.66x10$^{-1}$ |
| Maximum photon count (s$^{-1}$) | 3.98x10$^{18}$ | 5.35x10$^{18}$ |
| Measured edge photon flux (m$^{-2}$s$^{-1}$) | 7.77x10$^{19}$ | 1.11x10$^{20}$ |
| Measured edge photon count (s$^{-1}$) | 7.75x10$^{14}$ | 1.10x10$^{15}$ |
| Waveguide efficiency $\eta_c$ (%) | 0.02 | 0.02 |

Measuring QT1604 with dimensions 5mm x5mm x0.5mm with two different laser power settings. The maximum photon flux is calculated using Equation 3. The radiative efficiency is 0.85 and the EQE is 0.92 at incident wavelength of 532nm.

Preliminary studies with a Monte Carlo model suggest this very small cell waveguiding efficiency is due to the free carrier absorption in the highly doped substrate. Though small, $\eta_c$ can
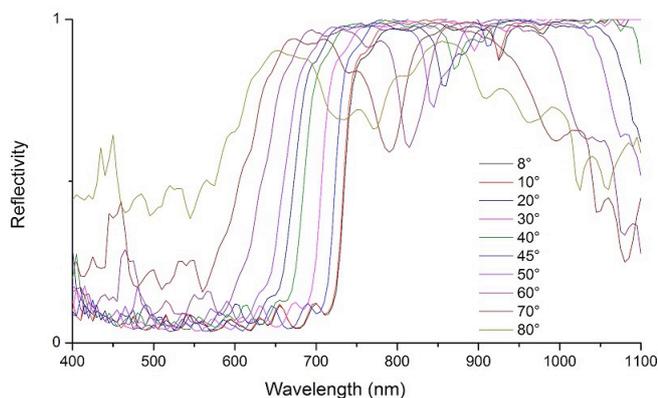
Fig. 8. Angular and wavelength dependence of the reflectivity of a hot mirror. Note the degradation of performance after the angle of incidence exceeds 60°.

be used to calibrate the Monte Carlo model using the edge measurements.

Using SOL, we can calculate the necessary QWSC waveguiding efficiency needed for ASTM G-173, 500x concentration light conditions when the QWSC is at maximum power point. An LSC with the parameters mentioned above under diffuse illumination will produce on the edges a photon count of $1.9 \times 10^{17} s^{-1}$.

Table II shows that this photon flux from the diffuse radiation absorbed by the LSC can be matched with the waste radiative emission from the QWSC even with the high resistance cell in Figure 6 as long as the cell waveguide efficiency is around 62%. The second column is more typical of an optimised concentrator cell. Methods of reaching these cell waveguide efficiencies is discussed in section IV.

TABLE II
CALCULATING THE NECESSARY WAVEGUIDING EFFICIENCY OF QT 16 04

| | High resistance | Low resistance |
|---|---|---|
| $J_{SC}$ at 500x concentration (Am$^{-2}$) | $1.28 \times 10^5$ | $1.28 \times 10^5$ |
| Series resistance ($\Omega$) | 0.22 | 0.03 |
| Voltage at MPP (V) | 0.998 | 1.016 |
| $J_{rad}$ at Vmpp (Am$^{-2}$) | 1103.25 | 2119 |
| $I_{rad}$ (A) | $5.41 \times 10^{-2}$ | $1.04 \times 10^{-2}$ |
| Max. Photon count (s$^{-1}$) | $3.38 \times 10^{17}$ | $6.49 \times 10^{17}$ |
| LSC waveguide efficiency (%) | 90 | 90 |
| QWSC waveguide efficiency (%) | 62 | 32 |
| Edge output (s$^{-1}$) | $1.9 \times 10^{17}$ | $1.9 \times 10^{17}$ |

Assuming a QT1604 solar cell dimension of 7mm x 7mm to match the LSC photon output of $1.9 \times 10^{17} s^{-1}$ at the LSC edge, using calculations for voltage at maximum power point and radiative current from SOL. The QWSC is calculated to be operating at maximum power point MPP, at 500x concentration in AM1.5D light conditions.

## IV. A BRIEF DISCUSSION ON OPTIMISATION

The calibrated Monte Carlo model will be used to optimise the structure of the QWSC to enhance the waveguide efficiency to the values in Table II without loss of cell power conversion efficiency. The most obvious improvement would be to remove the substrate as could be achieved in practice in a lift off

process. This would be predicted to give a significant increase in edge emission due to the removal of what is essentially a photon sink. Solar cell structures could be optimised to further improve its waveguiding capabilities. Due to having a high refractive index, a solar cell has the ability to act as a good LSC if other free carrier absorption is minimised. For example, adding a second lower-refractive index window layers into a structure would enhance transverse waveguiding to the edges. If these optical confining structures are doped for as to provide the built-in field there need not be any intentional doping in the GaAs and quantum well active region. Lessening the dimensions of the solar cell would further reduce the free carrier absorption rate. Further studies on the Monte Carlo model will lead to the identification of better waveguide designs.

To increase the optical efficiency of an LSC, progress needs to be made on novel luminescent materials. Recent challenges involve striking a balance between attempting to engineer a larger Stokes shift between the absorption and emission spectra of the luminophore in order to decrease reabsorption losses, without decreasing the luminescent quantum yields.

Wavelength selective mirrors present a bottleneck in the system performance due to the non-ideal reflection behaviour that occurs at large angles of incidence. A point to note is that this could be mitigated in part by the development of novel luminescent materials, especially in the design of anisotropic emission. Research is currently being undertaken in this area [13]. Hot and cold mirrors from Edmund Optics were purchased and a characteristion was performed of their reflectivities as a function of angle and wavelength. Results are shown in Figure 8.

## V. CONCLUSIONS

The authors have presented a novel way to manage radiative losses from a quantum well solar cell (QWSC) and diffuse light, with the objective being to power a doubly-illuminated photoelectrochemical reactor to produce $H_2$. A QWSC is embedded in a luminescent solar concentrator (LSC), where light generated from radiative recombination escapes from the edges of the QWSC and trapped in the LSC through total internal reflection. The LSC absorbs diffuse light and traps re-emitted light. Wavelength selective mirrors are used to direct these two photon streams to their desired output edge. The design of the QWSC is a critical factor in enabling the efficient waveguiding and transmission of the radiative light out of its edges. Raytrace modelling from an in-house raytracer will be used to determine the performance of the whole optical setup.

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