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1200% ENHANCEMENT OF SOLAR ENERGY CONVERSION BY ENGINEERING THREE DIMENSIONAL ARRAYS OF FLEXIBLE BIOPHOTOELECTROCHEMICAL CELLS IN A FIXED FOOTPRINT ENCOMPASSED BY JOHNSON SOLID SHAPED OPTICAL WELL.

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ABSTRACT

Photosynthetic proteins carry out photochemical charge separation with a near-unity quantum efficiency and provide interesting materials for sustainable solar energy conversion in man-made photoelectrochemical devices. The three-dimensional architectures of natural photosynthesisers on both macroscopic and microscopic length scales contrast strikingly with the essentially two-dimensional architectures of commercial photovoltaic devices. In this work we fabricated flexible and semi-transparent bio-photoelectrochemical cells (BPEC) that showed excellent flexibility and durability in response to repeated mechanical deformation. A three-dimensional stack of five such BPECs connected in parallel produced a peak photocurrent of 2900 nA under simulated sunlight in the laboratory and 2400 nA when tested outdoors. Placement of the BPEC stack within either a regular solid reflective well or a Johnson solid reflective well further boosted these photocurrents, computational analysis indicating that the strongest boost that more than doubled output was the consequence of multiple reflections within the Johnson solid that increased the light intensity incident on the BPEC stack. These design features, inspired by natural structures for absorbing and reflecting sunlight, improved the relative performance of the BPECs under non-peak insolation, such that the photocurrent output under natural sunlight was relatively uniform between 10 am and 5 pm. We discuss how the flexibility, durability and partial transparency of the individual BPECs enables the fabrication of cell arrays with a range of three-dimensional architectures.

Keywords: Photosynthetic protein, bio-photovoltaics, flexible electrodes, Johnson solid, optical wells, three-dimensional architecture.

INTRODUCTION

Mankind is currently addressing concerns over future energy supply by transitioning from a dependence on fossil fuels, the fruits of ancient solar energy capture by photosynthetic organisms, to sustainable solar energy harvested through a variety of approaches that include photovoltaic and photoelectrochemical devices. The current dominant technology, two-dimensional silicon-based photovoltaic (PV) solar panels, provides interesting contrasts with the three-dimensional approach to the harvesting of sunlight adopted by photosynthetic organisms. The most obvious of these is at the macroscopic level. Commercial solar panels are typically arranged in two-dimensional arrays of relatively thin silicon photovoltaic modules such that sunlight that is transmitted, reflected or narrowly misses the module is not put to productive use. In contrast, photosynthetic organisms such as green plants arrange their modular photovoltaic elements (leaves) in multi-layered structures where sunlight transmitted through upper modules can be captured by lower modules. This natural three-dimensional approach also extends to the way photosynthetic structures are arranged at a microscopic level, a good example being the stacked membrane structures found in chloroplasts that house multiple layers of light-harvesting pigment-proteins.

It can also be argued that the three-dimensional approach taken by plants also assists in the capture of solar energy as the angle of incidence of sunlight varies across a day, a multiplicity of photosynthetic structures providing a means to better capture energy as the sun tracks across the sky. In contrast, the flat structure of fixed PV panels means that the angle of incidence of sunlight varies strongly across a day, and although sun-tracking systems are available¹ they are often not economical or practical for PV panels attached to houses or larger buildings². Over the last decade, a number of attempts have been made to develop three-dimensional photovoltaic structures (**Figure S1**, Supporting Information) with a view to increasing the energy density produced, diminishing concerns over practicable locations for PV arrays and lowering the overall cost of solar energy conversion².

In addition to the architectures of photosynthetic organisms inspiring a re-think of macroscale PV structures, the components of their photosystems have contributed to the development of new photosynthetic materials both indirectly, by guiding the design of man-made materials, and directly through the provision of sustainable materials for biohybrid solar

energy conversion. Regarding the latter, a variety of photosynthetic protein complexes from plants, cyanobacteria and purple photosynthetic bacteria have been adsorbed onto electrodes and incorporated into bio-photoelectrochemical cells (BPECs) for solar energy conversion, solar fuel synthesis and a variety of sensing technologies³⁻⁷. One of the most extensively used systems is the reaction centre (RC) and reaction centre-light harvesting 1 (RC-LH1) pigment-protein complexes from the purple bacterium *Rhodobacter (Rba.) sphaeroides* that absorb sunlight across a broad range from 200 to 1000 nm⁸⁻¹⁰. These proteins have been used to fabricate a wide range of BPECs and coated electrode systems, including examples that are relevant to the present work employing polyethylene terephthalate indium tin oxide (PET-ITO) as a working electrode^{11, 12}, platinized counter electrodes¹³ and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) as a redox mediator.^{13,}

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In this work, natural solar-harvesting components in the form of RC-LH1 pigment-protein complexes are combined with flexible and semi-transparent man-made electrode materials in a modular, three-dimensional photovoltaic architecture inspired by the macroscopic architecture of natural photosynthesis. The resulting structures overcome several limitations associated with simpler two-dimensional BPECs by more effectively exploiting available light energy both indoors and outdoors. Electrodeposition of Pt on a flexible polymeric electrode substrate is used as an economical way to fabricate a semi-transparent counter electrode for transparent, lightweight and flexible BPECs that can be assembled into a variety of three-dimensional solar cell arrays. The simple bioinspired strategy of passing transmitted or “near-miss” light back through a semi-transparent BPEC array using a variety of mirrored optical wells is shown to boost performance and, together with the three-dimensional architecture, mitigate against unwanted variations in photocurrent output as the sun tracks across the sky. An improved performance was recorded when the three-dimensional BPEC array was integrated with a regular solid optical well or, in particular, an optical well based on a Johnson solid.

RESULTS

To fabricate a flexible BPEC, a partially transparent PET-ITO film was used as the working (front) electrode. To form a suitable counter (rear) electrode, Pt was electrodeposited onto the same PET-ITO film for 60, 120, 180 or 240 s (see Experimental Procedures), producing a progressive reduction in transmittance (**Figure 1a**). Scanning electron microscopy (SEM) showed the presence of micron-sized platinum clusters uniformly distributed on the PET-ITO substrate (**Figure 1b**), the precise morphology of which (cluster diameter, surface roughness and coverage) depended on deposition time. After 240 s of electrodeposition, the Pt clusters covered the PET-ITO substrate almost completely (**Figure 1b**, right). The average transmittance of the bare PET-ITO substrate between 400 and 800 nm was ~80 % (**Figure 1c**) and this dropped gradually to ~67 % after Pt deposition for 240 s. Longer Pt deposition times were not explored as this would not have increased surface coverage but would have further reduced light transmittance, unnecessarily compromising BPEC performance.

Cyclic voltammetry (CV) of the four Pt-coated counter electrode materials in the presence of an iodide/tri-iodide electrolyte (**Figure 1d**) produced traces consistent with those obtained with a standard Pt electrode. Higher E_{ox} and E_{red} peak currents indicated that a better catalytic activity was obtained after deposition of Pt for 240 s than for shorter times. Linear sweep voltammetry (LSV) also established that an increase in Pt deposition time led to an enhanced catalytic current (**Figure S2**, Supporting Information). CV of this optimal electrode in the presence of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) revealed two well-defined, reversible oxidation peaks (**Figure S3**, Supporting Information) which could be attributed to the formation of di-cation (0.089 V; $\text{TMPD}^{*+} \leftrightarrow \text{TMPD}^{2+} + e^-$) and cation (0.49 V; $\text{TMPD} \leftrightarrow \text{TMPD}^{*+} + e^-$) states¹⁵. Again, this was consistent with traces obtained with a standard Pt electrode¹⁶.

The sheet resistance (R_s) of the four counter electrode materials were measured using the four-probe technique (**Figure 1e**). R_s dropped from ~19 Ω/cm^2 , for bare PET-ITO to ~8.4 Ω/cm^2 for the densest Pt coating, indicating an increased conductivity as coverage by Pt became more complete (**Figure 1b**). Charge transfer resistances (R_{ct}) were determined by electrochemical impedance spectroscopy (EIS) of dummy cells comprising two PET-ITO-Pt electrodes and TMPD as electrolyte. Nyquist plots of the EIS spectra (**Figure S4**, Supporting

Information) were fitted using an equivalent circuit model. As the Pt deposition time increased the value of R_{ct} decreased from 128 Ω/cm^2 to 101 Ω/cm^2 due to enhancement of the electron transfer process at the electrode/electrolyte interface (**Table S1** in Supporting Information).

The effects of deformation on the electrical properties of the platinized PET-ITO were examined through current-voltage curves measured for a single electrode (240 s deposited Pt) after multiple cycles of bending and relaxing (**Figure 1f**). The current-voltage relationship was found to be invariant even after subjecting the electrode to 800 deformations, a performance stability conducive to the fabrication of a flexible BPEC. Although conventional flexible electrodes obtained by sputtering or spin coating techniques tend to display delamination when subjected to strenuous bending or twisting cycles, these PET-ITO-Pt electrodes showed excellent performance stability with no visual delamination after 800 bending cycles.

BPECs were fabricated as described in the Experimental Section. Briefly, 25 μm -thick Surlyn thermoplastic film was used to create an approximately square cavity between a PET-ITO working electrode and PET-ITO-Pt counter electrode that was filled with a mixture of RC-LH1 protein as the photovoltaic component and TMPD and Q_0 as electrolytes. **Figure 2a** shows photo-chronoamperometry light on/off curves for four BPEC cells that differed the density of the Pt layer on the counter electrode; for convenience these cells are referred to as “60s”, “120s”, “180s” or “240s” to denote the time taken to deposit the Pt layer on the counter electrode. Photocurrents were measured under illumination through the front working electrode (**Figure 2a**, right) or rear counter electrode (**Figure 2a**, left); note - to enable the comparison in this plot the terminals were switched between illumination regimes. Illumination through the front electrode produced a photocurrent response of up to ~ 603 nA in the **240s** cell, the steady short circuit photocurrent (I_{sc}) increasing approximately linearly with the time taken to deposit the Pt layer on the counter electrode (**Figure 2a**, right). This indicated that I_{sc} was dependent on the electrical properties of the counter electrode and/or its interface with the electrolyte, increasing as the Pt coating became denser on the electrode surface. Identical illumination through the less transparent rear electrode also produced a I_{sc} with a linear dependence on Pt deposition time (**Figure 2a**, left), but with lower I_{sc} of up to ~ 450 nA consistent with poorer light penetration through the Pt-coated counter electrode.

For the **240s** device an open circuit voltage (V_{oc}) of 110 mV (± 5 mV) was obtained on illumination through the front electrode and 95 mV (± 7 mV) on illumination through the platinized rear electrode (data not shown).

An action spectrum of a single BPEC device illuminated through the front electrode showed a maximum external quantum efficiency (EQE) of $\sim 1.36\%$ at 860 nm, the line shape confirming that the photosynthetic protein was the source of the photo-response (**Figure 2b**). The suggested mechanism of this BPEC is as described in our previous work¹⁷ and is summarised in **Figure 2c**. Energy captured by the bacteriochlorophyll (BChl) and carotenoid pigments of the RC-LH1 complex produces photo-excitation of the primary electron donor BChl pair in the RC ($P \rightarrow P^*$), subsequent trans-protein charge separation reducing the Q_B acceptor ubiquinone. Q_0 , a water-soluble analogue of the native Q_{10} , likely mediates electron flow between the RC-LH1 quinone sites and the platinized counter electrode while TMPD likely mediates electron flow between the PET-ITO working electrode and the photo-oxidized RC primary electron donor BChls (P^+). Overall, the BPEC generates electric power from sunlight without undergoing any permanent chemical transformation. Based on previous work that showed that V_{oc} can be varied systematically¹⁸, the photovoltage generated by these flexible BPECs should depend on the relative energy levels of the TMPD and Q_0 redox mediators and the photo-oxidised primary electron donor in the photosynthetic protein.

The open-circuit voltage decay (OCVD) technique can be used as an effective method to determine the electron lifetime in a BPEC, and so explore charge recombination kinetics at the interface between the PET-ITO-Pt counter electrode and the TMPD redox mediator¹⁹. The technique involves monitoring the decay of the photovoltaic V_{oc} after turning off illumination that has created a steady-state, whilst maintaining open-circuit conditions. After applying this to the four types of BPEC the electron lifetime (τ_n) was calculated using²⁰:

$$\tau_n = \frac{K_B T}{e} \left(\frac{dV_{oc}}{dt} \right)^{-1}$$

where, (dV_{oc}/dt) is the first derivative of V_{oc} , parameter e is the positive elementary charge and $K_B T$ is the thermal energy. The rate of decay of V_{oc} is directly related τ_n because, as the illumination of the photovoltaic device at the open circuit potential is interrupted, excess electrons are diminished through recombination. The **240s** device showed higher electron

lifetimes compared to the other devices (**Figure S5a**), in accord with data on sheet resistance, conductivity and photo-chronoamperometry. The Tafel polarization technique was also used to provide insight into the interfacial charge transfer between the TMPD redox mediator and the counter electrode, to analyse the recombination dynamics and increasing photocurrent density of the BPECs^{20, 21 22}. The resulting plot of $\log(i)$ versus V is shown in **Figure S5b**. These data were fitted with the Butler-Volmer equation to determine the exchange current density (J_0) for each of the four devices (**Table S1**, Supporting Information). From these analyses it was concluded that the **240s** device possessed a higher exchange current density compared to the others, and that the value of this exchange current density was inversely proportional to the charge transfer resistance (R_{ct}) of the Pt-coated counter electrode.

An interesting option offered by electrodeposition is the possibility of depositing Pt on a pre-shaped substrate, and BPECs with such a shaped Pt layer were also constructed. Thermoplastic Surlyn film was used as a mask during a 240 s period of electrodeposition to form a shaped platinized surface (**Figure 3a**). The resulting electrode was fabricated into an RC-LH1 BPEC, again with TMPD and Q_0 as electrolytes. As with the unshaped **240s** device, this “**NUS**” cell produced a photocurrent of several hundred nA on applying 100 mW/cm² (1 sun) illumination through the working electrode (**Figure 3b**), the short circuit photocurrent declining to ~300 nA at 10 mW/cm² (0.1 sun) illumination (**Figure S6**, Supporting Information).

This patterned **NUS** device was used to investigate the effect of deformation on the output of the flexible BPECs and their mechanical durability. Manually bending the **NUS** device by ~45° and then allowing it to relax to a planar conformation had no effect on the magnitude of the photocurrent response (**Figure 3b**), although the time taken for the photocurrent to build was extended somewhat. The maximum output of the cell, measured when planar after being subjected to 50 bend/relax cycles, was unaffected up to 500 cumulative bend/relax cycles (**Figure 3c**), demonstrating excellent durability of structure and output. The cells could be deformed in a variety of ways by twisting, bending or wrapping around other objects (**Figure 3d**), and the effects on output of five repeated deform/relax cycles were examined with four such types of deformation (**Figure S7**, Supporting Information). The different BPECs showed some small variations in absolute output, but there were no significant effects of deforming the cells by bending or twisting.

In order to develop three-dimensional solar energy harvesting structures, the effects of connecting multiple **240s** BPECs in series or in parallel were investigated. In a planar, all-parallel configuration the photocurrent scaled linearly with the number of BPECs (**Figure 4a**; up to ~2800 nA for five devices), whereas in a planar all-series configuration the photovoltage increased as the number of modules increased (**Figure 4b**; up to ~610 mV for five devices). Five BPECs connected in parallel were then stacked using clear supports such that each device was arranged at approximately 90° relative to its neighbour(s) to minimise cell shading and to enhance the absorption of reflected and transmitted light (**Figure 4c,d**). This three-dimensional “BPEC stack” produced a maximum photocurrent of 2900 nA under 1 sun illumination from above and provided a maximum power density of 0.1375 $\mu\text{W}/\text{cm}^2$ (**Figure 4e**). Measurements conducted with illumination at different angles of incidence showed a good consistency in photocurrent output (**Figure 4f**), enabled by the transparent electrode and support materials and the thin layers of photoactive protein. This feature made the BPEC stack suitable for outdoor deployment, where the angle of incidence of direct illumination changes during the course of a day.

In addition to the advantage that a BPEC formed from two partially transparent electrodes can be illuminated through either electrode, and the advantage that light transmitted through one cell can be absorbed by another further along the light path, there is also the possibility for productive capture of transmitted or “near-miss” light if reflected back into the cells. To demonstrate this, sections of simple mirrored glass were used to fabricate five different geometrical designs of reflecting optical well and a conventional parabolic reflector was also used (see Supporting Information **Figure S8** for blueprints and **Figure S9** for images). The BPEC stack was placed in each of these (**Figure S10** in Supplementary Information) and illuminated from above using simulated sunlight in the laboratory. The first regular solid well (C1 - **Figure 5a, top left**) was a simple five-sided open cube with 50 x 50 mm sides and floor, producing a reflective area of 125 cm^2 . The photocurrent response of the BPEC stack without an optical well of ~2900 nA was increased by ~52 % by placement in cubic well C1 (**Figure 5b** and see **Table S2** in Supplementary Information) suggesting the conversion of additional light energy reflected into the BPEC stack. Well C2, a truncated square pyramid (**Figure 5a, top center**) was a five-sided reflective bowl with a 50 x 50 mm floor and four equal isosceles trapezoid sides. This increased the area

of the aperture through which light entered the well housing the BPEC stack to 120 x 120 mm and increased the reflective area to 148 cm². The photocurrent output of the stack was increased by ~39 % by placement in C2 (**Figure 5b** and **Table S2**), lower than that seen for the simple cube despite the increase in footprint of the well and the area of reflecting glass. However, the openness of the structure could have resulted in more reflective loss than the simple cubic structure.

To look at a means to enhance the photocurrent whilst decreasing footprint, reflecting wells in the form of an elongated square pyramid, a square cupola and an elongated square bipyramid were fabricated. Each had the geometry of a Johnson solid, being made up from regular polygons. Well C3 was a 35 mm open cube, one wall of which was replaced with an open square pyramid structure comprising 35 mm equilateral triangles to give a reflective area of ~65 cm² (**Figure 5a, top right**). The rectangular footprint of this well was 20.9 cm², only 74% of that of the cubic well C1, and the upper aperture was only 70% that of C1. The photocurrent response of the BPEC stack was increased by ~86% by placement in well C3 (**Figure 5b**), despite it having a smaller footprint, aperture and area of reflective glass than either of the regular solids C1 or C2. Well C4 was made up from five equilateral triangles and four squares to make an octagonal bowl (**Figure 6a, bottom left**). The squares and equilateral triangles had 50 mm sides. This structure possessed a high reflective area of 168 cm² and provided an enhancement of 135 % (**Figure 5b**). This strongly enhanced performance can be attributed to the combined effect of higher reflective area, optical volume and presence of inclined reflective triangles which directed light to the BPEC stack. Well C5 was a 35 mm open cube in which two opposing walls were replaced with an open square pyramid structure comprising 35 mm equilateral triangles. The structure had a reflective area of 68.6 cm² and gave a 76 % enhancement (**Figure 6b**). The origin of the higher boost provided by the Johnson solid shaped optical wells is explored below. Additionally, a conventional parabolic reflector of area ~720 cm² was used to test the 3D BPEC, and was found to produce an enhancement in the photocurrent of ??%, lower than any of the Johnson solids.

Single and stacked **240s** BPECs were also tested under outdoor conditions during days with uninterrupted bright sunlight. Under continuous monitoring a single BPEC device gave a maximum photocurrent of ~500 nA around midday, the current building as the intensity of incident sunlight increased in the morning and declining as it decreased in the afternoon

(**Figure 5c** and **Table S2**). The maximum output of the three-dimensional five BPEC stack was around five-fold higher at ~ 2550 nA, as expected (**Figure 5c**), but it also showed a much flatter spectral response across the middle part of the day than that of the single BPEC, likely because it was less sensitive to changes in the angle of incidence as the sun tracked across the sky due to the transparency of the cells and their 3D arrangement. A flat array of five BPECs connected in parallel produced a similar output of 2590 nA, but for a ~ 5 -fold greater footprint (**Table S2**)

In agreement with findings under laboratory conditions, placement of the five BPEC stack in any of the five optical wells produced a higher photocurrent, with all three wells with a Johnson solid geometry producing a larger enhancement than the remaining regular solids or parabolic reflector, and in the same $C4 > C3 > C5$ order (**Figure 5c** and **Table S2**). Relative to the footprint of a single BPEC, the maximum photocurrent density increased by $\sim 520\%$ when a vertical stack of five BPECs was used (for approximately the same device footprint), and by $\sim 1200\%$ when this stack was placed in the Johnson solid shaped optical well C4 (**Table S2**). For wells C1, C3, C4 and C5, the four giving the highest enhancements, the increase of the absolute photocurrent also seemed to be associated with an enhancement of the flatness of the current profile during the middle of the day compared to that achieved with the unmodified BPEC stack (**Figure 5c**).

The reflective properties of the five wells were analysed using the illumination analysis package TracePro[®] which integrates Monte Carlo ray tracing, analysis, CAD models, and optimization techniques to obtain solutions for illumination design and optical analysis. Geometric models were created using Unigraphics NX 10.0 software (**Figure 6a, c, e, g, i**) and imported as STEP (Standard for the Exchange of Product) models into Tracepro[®]. They were then converted into opto-mechanical models by giving properties to the surfaces. The surface to be analysed, the base of each well where the BPEC was placed, was assigned as “diffuse white” whereas the interior faces surrounding it were assigned as perfect mirrors and all exterior faces as perfect absorbers. The rectangular planar light source used for illumination was scaled to be larger in area than each opto-mechanical model and was oriented parallel to the base of each optical well at a distance of 6.5 mm from the upper aperture. Light at 500 nm (flux 300 W or 119048 W/m² incident intensity) emanated normal to this surface. A total of 1,000,000 incident rays were traced through each model to find the energy distribution across the base surface, this being represented as an irradiance map of absorbed flux (**Figure**

6b, d, f, h, j). The black rectangle indicates the approximately 7.2 cm² footprint of the 5 BPEC stack. Light hitting the base of each well was the sum of the directly incident light and light reflected off one or more walls. The average irradiance across the base of C2 of 416 W/m² was lower than the 948 W/m² obtained for C1, likely due to the openness of the structure and hence more reflective losses (see below). In contrast, the average irradiances across the base of the Johnson solid wells C3, C4 and C5 were all much higher at 1480, 1964 and 1209 W/m², respectively, effects attributable to reflection of light down into the structure by mirrors positioned at different favourable angles. These results were in accordance with the higher photocurrents obtained in experimental measurements both indoors and outdoors, indicating that the photocurrents obtained depended directly on the ability of the optical wells to intensify the light reaching the BPEC stack.

The same analysis was applied to the parabolic reflector (**Figure S11, right**). Optical simulation showed that incident rays were concentrated to a single point F (**Figure S11, left**) with no light distribution elsewhere. As shown in this simulation plot, the intensity of light was zero at all points except at the point F (60000 W/m²) and so only a single cell coincident at this point would receive reflected light.

DISCUSSION

Photosynthetic proteins, membranes, organelles, cells and tissues offer interesting alternative materials for solar energy conversion in a biohybrid setting. Aside from their natural abundance, these materials offer potentially biocompatible and sustainable routes to the fabrication of a wide range of devices¹¹. Additionally, the fundamental reactions of natural solar energy conversion, energy transfer during light harvesting and charge separation during energy trapping and conversion, occur with a very high quantum yield (event per photon), albeit at the expense of free energy. In the particular case of isolated photosynthetic proteins, the bulk of research into their use in a photovoltaic or photoelectrochemical context has concerned controlling the interactions between photoproteins and electrode or electrolyte materials, and the mechanisms through which these proteins can be used to generate photocurrents or photovoltages^{3, 5-7, 17, 23}. More recently, attention has begun to shift towards

the fabrication of actual BPEC devices and exploration of their potential use for solar energy conversion and also for a range of sensing applications^{24, 25, 26-28}

The present work explored combining photoproteins with flexible and transparent electrode materials for solar energy conversion within architectures inspired by natural photosynthesisers. To differentiate the working and counter electrodes, PET-ITO was platinized by electro-deposition. Pt was selected for its excellent catalytic activity (oxidation-reduction of redox mediator), an attribute that has led to its widespread use as a counter electrode material to boost device performance. Pt electrodes are commonly fabricated through chemical reduction²⁹, thermal evaporation³⁰, magnetron or electro-sputtering³¹ and electrophoretic deposition^{32, 33}, but most of these methods are not well suited to the fabrication of flexible electrodes. The electrocatalytic activity of a flexible counter electrode can be compromised by chemical reduction methods due to presence of the organic reagents used for improving adhesion between the Pt coat and the flexible substrate³⁴. Thermal evaporation requires higher calcination temperatures which may lead to degradation of the polymers present in the flexible substrate³⁵, and electro-sputtering requires an ultra-high vacuum to deposit thin layers³⁶. By comparison, electrophoretic deposition is an uncomplicated and cost-effective alternative which does not require a high temperature or vacuum and it is well suited to platinizing a flexible electrode substrate. It also enables patterning of the electrode active area. In the present work it was found that the density of Pt on the surface of the counter electrode was key to optimal operation of the flexible BPEC, a longer deposition time producing a surface with good catalytic activity and conductivity that supported higher photocurrents.

Importantly, although the layer of Pt deposited after 240 s of electro-deposition gave the best (photo)electrochemical and electrical results, the resulting counter electrodes remained ~60-70 % transparent to light across the visible and near-IR. This enabled the fabrication of a stacked array of five BPECs in which the lower cells were only partially shaded by the upper cells. In the laboratory, this stack showed a uniform response to illumination irrespective of its angle of incidence, and in contrast to results with a single cell the stack also showed a uniform response to outdoor illumination during the middle part of the day. The relatively flat response between ~10 am and ~5 pm likely indicates that self-shading is greatest when the sun is highest in the sky, producing an output that doesn't simply correlate

with light intensity (as was seen for a single cell). It is well known that flat panel solar cells need tracking hardware and software to work at optimal efficiency, however a three-dimensional array of partially transparent cells could provide an alternative approach to solar energy conversion without any requirement for sophisticated hardware for sensing or tracking. A 3D BPEC stack can also absorb more light and produce a consistently higher output than a planar BPEC of the same area footprint, which could prove more useful in circumstances of low light intensity or limited land space.

In addition to the formation of stacked structures, the excellent mechanical robustness of the PET-ITO-Pt electrode material and assembled BPECs opened a route to the fabrication of BPEC arrays with more complex three-dimensional architectures in which individual cells are bent or twisted and also could experience transient deformation. **Figure S12** in Supporting Information shows example prototype small and large hemispheres and a heart-shaped 3D array, each consisting of 10-20 flexible BPECs electrically linked with combinations of serial and parallel connections. These have potential for both outdoor use and, as illustrated in **Figure S12d**, indoor use. Indoor applications may be a particularly fertile area for devices based on proteins as natural photosynthetic systems have evolved to operate within a relatively narrow window of temperatures and, in many cases including purple photosynthetic bacteria, at relatively low light intensities.

A potential drawback of a relatively thin film photoelectrochemical cell is that much of the incident sunlight is not absorbed and, if the cell is transparent, is transmitted through the cell. As illustrated here, one way to mitigate against this is to fabricate three-dimensional layered arrays in which there is the possibility of light transmitted through upper cells being harvested by lower cells, mimicking light harvesting by the multi-layered leaf structures of plants. This enables connected BPECs to have a smaller footprint. In addition, the reflection of light transmitted through all or part of a BPEC stack, or narrowly missing it, provides a means to further boost photocurrent output. To demonstrate this, five reflecting optical wells made from simple mirrored glass were fabricated, with a view to redirecting near-miss light through the BPEC stack (**Figure 7**). The open 50 mm cube (C1) produced a 52 % increase in photocurrent from the BPEC stack but the wide aperture bowl (C2) made from an ~18% greater area of reflective mirror produced only a 39 % increase, despite the greater reflective surface and a nearly six-fold increase in footprint. Optical ray tracing indicated that both

reflective wells were relatively ineffective at directing light through the stack rather than out of the assembly, particularly the C2 bowl (**Figure 7**). In contrast a Johnson solid well comprising an elongated square pyramid (C3) produced an 86% increase in photocurrent despite being made from a much smaller area of mirror than either regular solids, and a well with two pyramidal sides (C5) produced a similar result. Optical ray tracing indicated that these were more effective at directing light into the BPEC stack (**Figure 7**). The most effective Johnson solid structure was a nine-f square cupola (C4) which produced 135 % increase in performance. This was mainly due to its higher reflective area and inclined reflecting triangular walls which directed the reflected light into the stack (**Figure 7**). It can be envisaged that further elaboration of the stacking of BPECs and optimisation of reflective structures could further boost the photocurrent that could be derived from a given device footprint. In densely populated cities where land area is limited, it would be vital to have an effective architecture with minimal footprint. The 3D stack array of BPECs provided an effective combination of footprint and device performance.

Returning to the theme of nature as a source of inspiration, photosynthesis in general does not employ reflection as a strategy to boost light capture, although the iridoplasts of certain shade-loving plants such as *Begonia* contain photonic structures formed from ordered photosynthetic membranes that enhance the absorption of green light³⁷. However the vision of many animals is enhanced by a reflective layer in the eye known as the *tapetum lucidum* that provides photons with a second opportunity to be absorbed by rhodopsin in the retina³⁸. This has particular utility in nocturnal and deep sea animals and is perhaps best known from the strong reflections often captured in flash photographs of domestic cats and dogs. Several studies have been reported that were aimed at boosting efficiency and overcoming limitations in thin film solar cells by using textured Si, Ag or one-dimensional photonic crystals to trap transmitted light which would otherwise be lost³⁹⁻⁴¹. However, such solutions often require sophisticated fabrication procedures and/or are expensive. As an alternative, in the present work optical wells based on simple mirrored glass were shown to boost the photocurrent output of the three-dimensional BPEC stack by reflecting transmitted light and so increasing the optical path length and intensity of light incident on the cells⁴². Such reflectors could be integrated with other partially transparent photovoltaic devices to develop economic alternatives for conventional metallic reflectors⁴³.

CONCLUSIONS

We have successfully demonstrated a simple low-footprint BPEC array that draws upon two features of natural photoresponsive systems, namely a three-dimensional architecture inspired by natural photosynthesis that places multiple light-harvesting units along the light path, and optical wells inspired by the reflective structures in the eyes of nocturnal animals that redirect unabsorbed photons through the light harvesting layers. A crucial component of these BPECs, the counter electrode, was prepared and optimized by electrodeposition of platinum on a flexible polymer substrate without any conventional heat treatment. The output of the assembled three-dimensional BPEC stack showed good uniformity of output at different angles of incident light in indoor trials. In outdoor trials the output was relatively flat between 9 am and 5 pm, and under both conditions the output was boosted by reflecting light back through the BPEC stack using simple mirrored glass in a variety of shapes. The elongated square pyramid, square cupola and elongated square bipyramid optical wells, constituting the Johnson solids, were particularly effective at boosting the photocurrent output of the BPEC stack whilst minimising the footprint of the well. In addition, the flexibility and good mechanical durability of the electrode materials and assembled cells facilitated the assembly of prototype devices with more complex three-dimensional architectures. We anticipate that our findings pave the way for new designs of photoelectrochemical cells with improved efficiency that exploit natural strategies for enhanced solar energy harvesting.

EXPERIMENTAL SECTION

Materials and Reagents

PET-ITO of surface resistivity 60 Ω/sq (Sigma-Aldrich) was used as the working electrode and the substrate for the counter electrode. Analytical reagent grade LiClO_4 , TMPD (99%), Q_0 (2-3-dimethoxy-5-methyl-*p*-benzoquinone, 98%), sealing materials (Surlyn; thickness 25 μm) and chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$; $\geq 37.5\%$) were purchased from Sigma-Aldrich and used as received. Organic solvents were purchased from Sigma-Aldrich and were purified by vacuum distillation.

Pt Electrodeposition and Electrode Characterization

Platinum was electrodeposited onto a PET-ITO substrate from an aqueous solution containing 0.0204 g chloroplatinic acid (5 mM) and 0.1063 g lithium chloride dissolved in 10 mL distilled water (0.1 M). A cell comprising an FTO glass electrode (anode, negative potential) and PET-ITO electrode (cathode, positive potential) was used. Before electrodeposition, both conducting substrates were cleaned using surfactant, distilled water and ethanol, sequentially. The two electrodes were immersed vertically into the deposition solution at a separation of 1.5 cm. Platinum deposition was achieved by application of a constant current density of 1 mA for 5 s followed by 0.9 mA for either 60, 120, 180 or 240 s. After deposition electrodes were initially dried in air and then heated in a vacuum oven at 60°C for 3-4 hrs.

SEM using a Zeiss Supra 40 FE was used to analyse the surface morphology of the resulting PET-ITO-Pt substrates. Their catalytic properties were initially screened by CV using an Autolab FRA32 electrochemical interface system at a scan rate 10 mV/sec. The electrochemical cell consisted of PET-ITO-Pt, Pt-wire and non-aqueous Ag/AgCl as the working, counter and reference electrode, respectively. Electrolytes were either 10 mM TMPD and 0.1 M LiClO₄ in 10 mM Tris-HCl buffer (pH 7.5) or 5 mM LiI, 0.5 mM I₂ and 0.05 M LiClO₄. LSV was measured using a two-probe technique to monitor the conductivity changes during different mechanical deformation stages. The sheet resistance (R_s) of the platinized PET-ITO electrodes was measured by using four-probe conductivity meter. EIS was carried out using the Autolab FRA 32 interface. Two symmetric dummy cells (Pt-PET-ITO/redox mediator/Pt-PET-ITO) were fabricated and the tests were conducted using a low amplitude AC signal of 10 mV in the frequency range of 100 KHz to 0.1 Hz. Data were fitted using an equivalent circuit model. The transmittance of electrode materials and the absorbance of the photoprotein solution were measured using a Shimadzu UV-Vis spectrophotometer.

RC-LH1 photoprotein

RC-LH1 complexes lacking the PufX protein were isolated from photosynthetic membranes using the detergent n-dodecyl β -D-maltopyranoside (DDM), and purified as described previously^{17, 44}. Protein was stored at -80 °C as a concentrated solution in 20 mM Tris (pH 8.0)/0.04% (w/v) DDM until use. Structural models of PufX-deficient RC-LH1 complexes are based on the X-ray crystal structure of the similar complex from *Thermochromatium tepidum*.⁴⁵

Cell Fabrication and Characterization

For the **240s** and related cells the PET-ITO to be used as the working electrode (designated the front electrode) was cleaned by sonication in acetone and then in isopropanol. PET-ITO-Pt produced by electro-deposition of Pt for various times was used as the counter electrode (designated as the back electrode). Thermoplastic Surlyn film of 25 μm thickness was cut to form a square cavity. A 5 μL aliquot of a mixture of 85 μM photosynthetic RC-LH1, 80 mM Q_0 and 250 μM TMPD was injected into the cavity between the electrodes and the cell sealed with epoxy resin. Cells of overall dimensions of 2 cm X 1.5 cm were fabricated.

For the **NUS** cell a PET-ITO substrate of dimension 3 cm X 2 cm was taken, and a photomask made of Surlyn film was fabricated with the letters NUS carved out of it. The mask was placed on top of PET-ITO substrate and electro-deposition of Pt was carried out to obtain the shaped Pt electrode.

A Newport Solar Simulator and a Keithley 2400 source meter were used for the photo-chronoamperometry. Front and rear side illumination was with white light (100 mW cm^{-2}). For EQE measurements, light from a quartz tungsten halogen lamp was dispersed through a monochromator and the output focused onto the cell. No area constraints were maintained for any electrochemical measurements as being a liquid cell, there would be an instantaneous change in the area under bending conditions. However, all the devices in the stacked BPECs had an average active area of 70 mm^2 .

3D BPEC fabrication and construction of the optical wells

Five flexible **240s** RC-LH1/TMPD/ Q_0 BPECs fabricated as described above were connected in parallel in a stacked structure supported by glass slides that formed sides and a base. Each BPEC was positioned at 45° to its neighbour(s). Gold (250 nm) was sputtered onto the supporting glass slides to ensure connectivity between the BPECs.

To fabricate the optical wells, mirrored glass was cut into 50 mm X 50 mm squares. Five of these were attached to one another using a hot glue gun to form the cubic reflecting optical well C1, giving an internal volume of $\sim 125 \text{ cm}^3$ and a reflective area of 125 cm^2 . For well C2, four mirror walls in the shape of isosceles trapezoids of 50 mm x 50 mm x 50 mm x 120 mm were glued at an angle of 45° to a fifth mirror of 50 mm X 50 mm which formed the floor, producing a five-sided bowl of depth 36.2 mm. This well had an internal volume of $\sim 276 \text{ cm}^3$

and a reflective area of 148 cm². To fabricate Johnson solid C3, three mirror walls of 35 mm x 35 mm were joined to a 35 mm x 35 mm base. The remaining side was constructed using three 35 mm equilateral triangular pieces of mirror to form a square pyramid that was open on one side. The resulting structure was an elongated square pyramid with an internal volume of ~53 cm³. To fabricate Johnson solid C4, five squares and four equilateral triangles of side 50 mm were joined together to form the square cupola shape. The sides were at an angle 45° to the base square. The structure presented a volume of 242.85 cm³. Smaller sides were not used for the square cupola as this would not allow the stack to sit completely inside the optical well. In case of Johnson solid C5, two facing walls from a 35 mm cube were removed and each replaced with three 35 mm equilateral triangular pieces of mirror to form three sides of a square pyramid. This structure had an internal volume of 63.14 cm³. The parabolic reflector was purchased from RS electronics and had an outer diameter of 10 cm and a depth of 5 cm (**Figure S8**).

Prototype three-dimensional BPEC array shapes were fabricated using 10-20 **240s** cells connecting either in series or in parallel using copper tape.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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Figure 1. Flexible counter electrode fabrication and characterization. (a) Counter electrodes formed by electro-deposition ($I = \sim 1$ mA) of Pt on a PET-ITO substrate for (left to right) 60, 120, 180 or 240 s. Electrodes were imaged against a coloured background to show the effect

on transparency. (b) Surface morphologies of the four platinized PET-ITO substrates examined by SEM. (c) Transmittance spectra of the four platinized PET-ITO counter electrodes and plain PET-ITO. (d) Cyclic voltammograms of the platinized counter electrodes against an iodide-triiodide redox couple (5 mM LiI, 0.5 mM I₂ and 0.05 M LiClO₄). (e) Sheet resistances of plain PET-ITO and the platinized counter electrodes. (f) Linear sweep voltammetry of a platinized counter electrode before and after multiple twisting and bending cycles.

Figure 2. BPEC performance and mechanism. (a) Photocurrent responses obtained from four BPEC devices when illuminated through the front working electrode (right) or rear platinized counter electrode (left). The devices differed in the density of Pt on the counter electrode, determined by the Pt deposition time. To create the plot the polarity of the measuring system was swapped between front and rear illumination for each device. (b) EQE action spectrum for a **240s** BPEC device compared to the solution absorbance spectrum of the RC-LH1 complex. (c) Energy level diagram for the BPEC.

Figure 3. Flexible BPEC fabrication and performance. (a) Preparation of an electrode with a predesigned shape on a flexible substrate using the electro-deposition technique. (b) Normalized photocurrent response of a **NUS** BPEC measured before and after a single bend/relax cycle. (c) Photocurrent density from a **NUS** BPEC measured before and after ten sets of fifty bend/relax cycles. (d) Assembled flexible **NUS** BPECs undergoing different mechanical deformations.

Figure 4. Photoelectrochemical characterisation of connected BPEC arrays. (a) Photocurrents from one to five **240s** BPECs in connected in parallel. Orange shading indicates the period of illumination. (b) Increasing photovoltages from one to five **240s** BPECs connected in series. (c) Fabricated stack of five **240s** BPECs connected in parallel. (d) Schematic of the stack of five **240s** BPECs. (e) Power generated by the stack of five **240s** BPECs. (f) Photocurrent responses of the five **240s** BPEC stack as a function of the angle of illumination, simulating varying illumination across a 12 hour day for angles between 0° and 180°.

(a)

(b)

(c)

Figure 5. Effect of optical wells on performance of the five BPEC stack. (a) Trimetric views and top-down images of reflective wells C1 (top left), C2 (top center), C3 (top right), C4 (bottom left), C5 (bottom center) and the parabolic reflector (bottom right). (b) Effects of the reflective wells on the photocurrent from the five BPEC stack under simulated one Sun illumination; the photovoltage from the BPEC stack was 105 mV. (c) Photocurrent measured during a single sunny day in Singapore for a single BPEC device and the five BPEC stack without or with one of the five optical wells (C1-C5) or the parabolic reflector (para).

Figure 6. Optical analysis and simulation. (a), (c), (e), (g) and (i) show optical STEP models of reflective wells C1, C2, C3, C4 and C5, respectively. (b), (d), (f), (h) and (j) show corresponding irradiance maps obtained using Tracepro® software showing areas of low to high irradiance when traced using 1000000 incident rays (the black square box indicates the 7.2 cm² footprint of the five BPEC stack within the well).

Figure 7. Schematic illustrations of light reflection in the optical wells. The representation of a device in the wells is not to scale.