Electrohydrodynamically printed solid-state Photo-electro protein micro-capacitors

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Abstract

The rapid development of portable and scalable electronics requires the production of high-performing, miniaturized energy storage devices with great flexibility and dimensional liberty. In recent years, printed capacitors have emerged as a promising means of meeting these demands. Printed flexible solid-state capacitors are being considered as next-generation energy storage systems because of their flexibility, portability, low cost, scalability, long cycle stability, and the option of charging or discharging securely. Here we use sustainable and toxin-free photosynthetic protein complexes to fabricate solid-state flexible Photo-electro micro-capacitors as flexible power packs that are operable under indoor illumination. Electrohydrodynamic (EHD) printing was used to print biohybrid Photo-electro protein micro-capacitors that exhibited high performance uniformity and operational stability. Devices could be connected in either series or parallel configurations to modulate the operating voltage window and charge-discharge time. A specific capacitance of 110 mF g\(^{-1}\) was obtained at a scan rate of 10 mV s\(^{-1}\) and was retained at 91% of the initial value after 10,000 charge/discharge cycles at a current density of 0.063 mA g\(^{-1}\). Devices also displayed mechanical stability and robustness, retaining 93% of initial capacitance after 1000 cycles of bending. The data demonstrate that these micro-capacitors can deliver an economical and practical option as flexible energy storage and delivery devices for applications where exposure is primarily to indoor light.

1. Introduction

Energy storage devices such as capacitors, photocapacitors, fuel cells and batteries play key roles in a plethora of technological applications [1–3]. However, such devices are often bulky and/or heavy, and struggle to meet growing demands for power supplies that are lightweight, flexible and, increasingly, formed from renewable or biodegradable components. In recent years researchers have worked towards developing thin, flexible and compact energy storage systems that can meet the demand for technologies such as wearable electronics [4–7]. Flexible capacitors have been considered as a potential component of smart wearables due to their durability, cycle stability and sustained performance under continuous mechanical deformation [8–10]. However, the design of devices with flexibility and shape versatility continues to be a significant challenge. Currently, flexible capacitors are fabricated using methods such as spin coating [11], the use of sol gels [12,13], electrochemical deposition [14–16], chemical vapour deposition [17,18] and a range of printing procedures such as extrusion [19,20], fused deposition moulding [21,22] and injection [23–25]. Many of these techniques involve prohibitive costs, long production times, low efficiency and complex processing methods that hinder the large-scale development of flexible devices [26,27].

Among these approaches, printed capacitors can bring potential advantages such as patterning, better design diversity, tuneable size, compact architecture and excellent flexibility [28–30]. As examples, Lee et al. have used UV curing assisted stencil printing to developed a printed capacitor consisting of an SiO\(_2\) nanoparticle-based electrolyte and activated carbon/multiwalled carbon nanotube electrodes. When printed on T-shirts the capacitor exhibited exceptional form factors, flexibility, and stability against laundering, wringing, ironing and folding [31]. Won et al. have fabricated an all-printed wearable, self-charging photocopacitor module made up of organic solar cells dubbed...
supercapacitors fibres. The woven photocapacitor module yield a voltage output of 3.2 V in ≈5 min under one Sun (100 mW cm⁻²) illumi-
ination, achieving a final photo-conversion-and-storage efficiency of 4.94% at a discharge current of 3 mA. The cells demonstrated a high
capacitance of ≈52 mF cm⁻² with an energy density of 12.5 μWh cm⁻², and up to 96% retention of capacitance after 5000 charge/discharge
cycles [32].

The main advantages of conventional capacitors and batteries are low production costs, long cycle life and the ability to be charged or
discharged securely [33–35]. However, they typically use materials that are toxic and/or non sustainable [36–38], creating issues at end of life
disposal. In addition, most energy storage devices use two different components for energy harvesting and energy storage. A progressive
step in this area would be to explore the use of green, non-toxic and sustainable materials which can harvest, store and distribute energy in
a single unit [39,40]. Candidate materials for this are natural pigment-protein biomacromolecules such as the “RC-LH1 complex” that
enables solar energy conversion by purple photosynthetic bacteria [41].

This well-characterised system consists of a hollow cylindrical light harvesting (LH) domain that captures solar energy and transfers an
excited electronic state to a central reaction centre (RC) which catalyses highly quantum-efficient photochemical charge separation [42].
The light harvesting “antenna” greatly enhances photon capture and energy conversion by the RC “transducer”, enabling photosynthetic growth at
the low light intensities found in the ecosystems these organisms inhabit. In a device setting the metastable charge separated state formed
by the RC (a radical pair term P Q) can either initiate a photo-
current in a bio-photoelectrochemical cell or provide a means to store
charge in a bio-photocapacitor (see Fig. 2e). Photosynthetic proteins are part of a broader range of natural materials that are of interest with
respect to the provision of eco sustainable energy [43–45]. For example, Shen et al. recently demonstrated the very first example of a
self-charging enzymatic supercapacitive biofuel cell to convert and store energy within a single device. The device possesses an operating regime
(4.5 and 0.3 μm cm⁻², respectively) with an 80% residual activity after 50 charge/discharge pulses [46]. Khairy et al. have developed super-
capacitors based on commercial 3D open-pore Ni foam and haem pro-
teins. When tested at 0.4 mA discharge current, devices based on haemoglobin, myoglobin and cytochrome c generated specific capaci-
tances of 13.8, 8.9 and 8.2 F g⁻¹, respectively [47].

A challenge in the design of biohybrid devices is the controlled deposition or patterning of the biomaterial on a supporting substrate or
electrode surface, and one approach to addressing this is printing using a biomolecule ink. Of the printing technologies available commerci-
ely, electrohydrodynamic printing (EHD) is the least explored for the patterning of biomolecules [48,49]. Inkjet printing, screen printing and
lithography are the most widely used technology in printed electronics. In Inkjet printing, ink is ejected from the nozzle by the pressure pulses
generated from piezoelectric or thermal or pneumatic actuation. The protein ink used in this manuscript is sensitive to temperature; and high
temperature leads to conformal disintegration of the protein molecules, making them no longer photoelectrochemically available/usable.
Furthermore, jetting printing requires specialized materials to be incor-
porated in the ink formulation to allow easy ejection of the ink. Another critical challenge of jet of its limited printing resolution, which is
restricted to 20 μm. Reports have showed that EHD is capable of printing structures as low as 2 nm. Screen printing is also commonly used tech-
nique used for high resolution printing. However, it requires special requirements on the ink in order to transfer the pattern. It also requires a
masque/stencil to fabricate the structures, which makes the printing process pretty time-consuming and expensive. Similarly, lithography
also do not offer a general approach to high resolution, and it requires additional patterning systems and processing steps to define the printed
structures. EHD printing technique exploits electrohydrodynamics to transfer ink from a nozzle to a substrate on a conducting X-Y stage by
applying a voltage difference between the two [50–52]. In comparison
to alternatives, the formation of protein micro-arrays by EHD printing has a number of advantages including being compatible with a large
substrate area, inexpensive, rapid, versatile, and enabling formation of very precise micro and nanoparticles due to minimization of lateral
variations in the droplet position as a consequence of distribution by the electric field [50,53]. The technique has been used to fabricate printed
capacitors with a high specific capacitance and energy density. For example, Lee et al. successfully fabricated an ultra-high areal number
density solid-state micro-capacitor directly on a chip using EHD printing that had an operating voltage of 65.9 V cm⁻² [54]. Researchers have
also used the technique to rapidly lay down highly uniform patterns of both single and multiple proteins over large areas [55]. Although re-
searchers have attempted to print DNA micro arrays and patterns of proteins using EHD printing for cell cultures, there has been almost no
attempt at using the technique to print photosynthetic proteins for functional applications like micro-photocapacitors. Deriving confidence
from the current observation of charge storage ability with photosyn-
thetic proteins, it can be attempted to design and print capacitors that

In this work, we have used EHD printing to fabricate a solid state,
flexible, biohybrid Photo-electro protein micro-capacitor (MC) that is
operable under the low intensity lighting that is typically found in in-
door settings. A micro-capacitor is a miniaturised, lightweight and
portable passive circuit component that stores electrical energy in the
form of electrostatic charges. It is widely used in microelectronics and
usually consists of a thin film of dielectric material sandwiched between electrodes. The advantages of a solid-state system include ease of
handling, scalability, increased safety and flexibility, high reliability,
and tolerance of a wide range of operating temperatures [56–58]. The
printed biohybrid MCs exhibited an optimal specific capacitance of 110
mF g⁻¹ at a scan rate of 10 mV s⁻¹ under only 0.002 Sun illumination,
and showed excellent mechanical flexibility and operational stability.
Cell voltage and charging-discharging time could be customised by
simply connecting multiple devices in series or in parallel. Such printed
solid-state devices show potential for the field of flexible, portable
wearable electrochemical energy storage systems involving sustainable
components.

2. Experimental

2.1. Materials

Non-conductive polyethylene terephthalate (PET) films were pur-
chased from a LaTech Scientific Supply, Singapore. Platinum and
tungsten inks were purchased from Sigma Aldrich. Distilled water (DI)
was used for all experimental and cleaning purposes. RC-LH1 complexes
lacking the PuX protein were purified as described previously using n-
dodecyl β-D-maltopyranoside (DDM) as the isolating detergent [59,60].
They were stored as a concentrated solution in 20 mM Tris (pH
8.0)/0.04% (w/v) β-D-dodecyl maltoside (DDM) at –80 °C prior to use.
Structural models of PuX-deficient RC-LH1 complexes are based on the
X-ray crystal structure of the similar complex from Thermochromatium
tepidum [61]. The concentration of RC-LH1 protein was such that the
absorbance at 874 nm was equivalent to ~690 absorbence units cm⁻¹.

2.2. Photo-electro protein micro-capacitor fabrication and
caracterisations

Non-conductive PET films were washed thoroughly by sonicating
continuously in ethanol for 30 mins, rinsed using DI water and dried.
Square platinum and tungsten electrodes (0.9 cm²) were printed at a
separation of 1.5 cm using commercial platinum and tungsten inks. In
this work, the working electrode (WE) is Platinum, which acts as a
cathode and the counter electrode (CE) i.e., Tungsten is required to
complete the electric circuit. The RC-LH1 protein solution was used for
printing without further modification (Supplementary Movie S1). Inks
were housed in a syringe connected to an Enjet (Korea) EHD printing system (Fig. 1a). A voltage in the range 1 to 5 kV was applied to the nozzle attached to the syringe pump to generate an electrostatic field between the nozzle and the substrate, resulting in the formation of a meniscus at the nozzle tip due to the surface tension of the ink. When the electric field stress exceeded this surface tension the meniscus elongated in the direction of the field lines, resulting in the formation of an ink jet (Fig. 1b). Separation of nozzle and substrate was fixed at 50 µm and printing speeds were between 5 and 25 mm/s with multiple passes. Loadings of RC-LH1 complexes for 7, 14, 21 and 35 printing passes were calculated to be 32, 41, 46 and 60 mg cm$^{-2}$, respectively, based on changes in mass of the substrate. Devices were dried for 5 mins under ambient conditions after printing.

2.3. Device characterization

Printing of protein complexes and electrode materials was carried out using an EHD printer (Enjet, Korea) with a digitally controlled pressure pump. Cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge/Discharge (GCD) measurements were carried out using a CHI 660 D electrochemical workstation under ambient laboratory light (0.002 sun). CV measurements

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Fig. 1. Device fabrication. a) Schematic of the EHD printing of a biohybrid MC comprising a Pt electrode, W electrode and a connecting RC-LH1 protein line deposited from the ink nozzle onto a PET substrate on an X-Y stage. b) Schematic of ink behaviour as a function of applied voltage. c) Width of the printed protein line as a function of the voltage applied between the nozzle and the X-Y stage. d) Image of the RC-LH1 protein lines achieved at different applied voltages. e) Width of the printed protein line as a function of printing speed. f) Image of the RC-LH1 protein lines achieved at different printing speeds. g) Thickness (depth) of printed protein lines and mass loading of RC-LH1 proteins as a function of the number of printing passes. h) Image of the RC-LH1 protein lines achieved with different numbers of printing pass.
were conducted in a voltage range of 0–1 V with voltage sweep rates from 10 to 100 mV/s. EIS was recorded over a frequency range of $10^{-1}$ to $10^3$ Hz at 0 V with an amplitude of 10 mV. GCD measurements were carried out at various current densities ranging from 0.013 to 0.08 mA cm$^{-2}$. Absorbance of the RC-LH1 protein solution was recorded using a Shimadzu UV–Vis spectrophotometer. Rheological tests were carried out using an Anton Paar modular compact rheometer (MCR302) with a parallel plate probe (PP25-SN 17002). Measurements were performed using 1 mL of sample in rotation mode. An Alpha Step D500 Profiler (KLA Tencor) was used to record the printed pattern thickness/height of the protein wire. The mechanical flexibility of the EHD-printed electrodes was quantitatively measured using a universal tensile machine (DA-01, Petrol LAB).

Specific capacitances ($C$, $F/g$) were calculated from the CV curves according to:

$$C = \frac{I\Delta V}{V \Delta t} \cdot (\text{mV})$$

where $I$ is the current density ($A/cm^2$), $\Delta V$ is the voltage range, $V$ is the potential ($V$), $\Delta t$ is the potential scan rate ($mV/s$), and $m$ is the mass of the electroactive materials in the electrodes ($g/cm^2$) [64].

Areal capacitances were calculated using:

$$C_{\text{areal}} = \frac{I\Delta V}{A \Delta V}$$

where $I$ is the current, $\Delta t$ is the discharge time, $A$ is the total area of the electrode, $\Delta V$ is the operating voltage window.

Volumetric capacitances were calculated using:

$$C_{\text{volumetric}} = \frac{I\Delta V}{V \Delta V}$$

where $V$ is the total volume of the device.

3. Results and discussion

Biohybrid Photo-electro protein MCs were printed on a non-conductive PET film substrate. They consisted of a single line of deposited protein connecting printed square platinum and tungsten electrodes that were 1.5 cm apart (Fig. 1a). Scanning Electron Microscopy (SEM) image of the EHD printed RC-LH1 protein ink on PET substrate shows that the ink printing is in the form of cylindrical pattern (Figure S1 in Supplementary Information). The protein ink was a concentrated solution of purified RC-LH1 complexes in 20 mM Tris buffer (pH 8.0)/0.04% DDM. This RC-LH1 ink showed sheer thinning behaviour, the viscosity decreasing with an increase in shear rate (Figure S2a in Supplementary Information). As a consequence of the bacteriochlorophyll and carotenoid pigmentation of the RC-LH1 complexes (Figure S2b in Supplementary Information) the ink provided light harvesting capacity in the near-ultraviolet, in the blue and green regions of the visible spectrum, and in the near infrared [62]. For effective EHD printing with the RC-LH1 ink and the inks used to print electrodes, a series of parameters were optimized (Table S1). It was found that varying the strength of the applied voltage used to discharge ink from the nozzle tip led to different jetting modes (Fig. 1b). At low voltages there was no discharge due electrostatic forces being too weak to overcome the surface tension of the liquid, and on increasing the voltage some micro-dripping was seen in which gravity assisted some droplet discharge from the nozzle tip [53]. When the applied voltage reached 1.8 kV a thin thread of liquid (cone jet) was ejected that formed droplet discharge from the nozzle tip [53]. When the applied voltage some micro-dripping was seen in which gravity assisted some droplet discharge from the nozzle tip. The behaviour of the ink from the nozzle tip led to different jetting modes (Fig. 1b). At low voltages there was no discharge due electrostatic forces being too weak to overcome the surface tension of the liquid, and on increasing the voltage some micro-dripping was seen in which gravity assisted some droplet discharge from the nozzle tip [53]. When the applied voltage reached 1.8 kV a thin thread of liquid (cone jet) was ejected that formed droplet discharge from the nozzle tip [53]. When the applied voltage some micro-dripping was seen in which gravity assisted some droplet discharge from the nozzle tip. The equivalent series resistance ($R_s$) and a Warburg resistance ($Z_w$) and a double-layer capacitance ($C_d$). Nyquist plots showed a straight vertical line segment in the low-frequency region that is typical of capacitive behaviour (Fig. 2d). The inclined line in the medium-frequency region above the knee frequency corresponded to the $Z_w$. The equivalent series resistance ($R_s$) was the X-intercept in the high-frequency region (Fig. 2d), and the radius of the plotted semicircle plotted was representative of the $R_s$. A gradual increase in $R_s$ and $R_{ct}$ with increasing protein line width (Table S2) indicated an increasingly unfavourable medium for ion diffusion, confirming the narrowest 280 µm width lines as being preferable.

The proposed mechanism of photoinduced charge storage is illustrated in Fig. 2e. Low intensity illumination produced photochemical charge separation inside the RCs creating electric dipoles throughout the protein array. As there is no electrolyte to efficiently transport these charges, oxidation at the tungsten anode and reduction at the platinum cathode results in the trapping of charge within the protein array, causing a potential across the device.

The influence of protein loading was examined by varying the number of EHD printing passes used to manufacture MCs. A broader CV curve was obtained for a device printed with 35 printing passes than devices formed from either 21, 14 or 7 passes (Fig. 3a) suggesting a dependence on the availability of RC-LH1 complexes to perform charge separation. Analysis of these CV curves revealed a linear increase in specific capacitance with an increasing number of printing passes (Fig. 3b). In Nyquist plots of EIS data on these devices (Fig. 3c) the values of $R_s$ and $R_{ct}$ were inversely dependent on the number of passes (Table S3), lines formed from 35 passes having the highest values indicative of the worst electron diffusion kinetics. As indicated above, CV curves for the 35 pass device measured under indoor light (0.002 Sun) at three different scan rates between 10 and 100 mV/s were nearly rectangular in shape and symmetric, characteristics typical of conventional capacitors (Fig. 2c). In contrast, CV curves for devices formed with 7, 14 or 21 printing passes were non-rectangular and only partly
Fig. 2. Device characterisation. a) CV profiles (scan rate 100 mV/s) for a standard MC under indoor light (0.002 Sun) and in the dark. b) CV profiles (scan rate 100 mV/s) at different voltages for a standard MC under 0.002 Sun illumination. c) CV profiles at different scan rates for a standard MC under 0.002 Sun. d) Nyquist plots of EIS data for MCs with different protein line widths. e) Outline of the mechanism of charge separation and photocapacitance generated by RC-LH1 complexes. Photoexcitation triggers charge separation with the RC component between the primary electron donor bacteriochlorophylls (P) and the secondary acceptor ubiquinone (Q_B). Charge separation is initiated by photoexcitation of P into its first singlet excited state (P^*), forming a P^+ cation at one “terminal” of the protein. Charge separation continues through the sequential formation of series of increasingly long-lived radical pairs (P^+ H_A, P^+ Q_A, and P^+ Q_B). At each stage, rapid onward electron transfer (green solid lines) kinetically outcompetes slow recombination processes (grey dash lines) ensuring a high quantum efficiency. The electron is transferred across the protein to form an anion at the ubiquinone (Q_B) at the other “terminal” of the protein [43]. In the absence of any electrolyte, minimal electron transfer from the tungsten electrode or to the platinum electrode would be plausible, with the majority of the charges trapped within the protein multilayers giving rise to the device’s capacitance.
symmetric (Figure S6 in Supplementary information), indicating less ideal behaviour. A single RC-LH1 complex has a maximum diameter of \( \sim 13 \) nm [40]. Hence, a printed pattern with 7, 14, 21 and 35 printing passes would contain \( \sim 150, \sim 500, \sim 650 \) and \( \sim 1170 \) stacked protein units respectively. Hence, more dipole units would be generated for the device with 35 printing passes compared to its counterparts. This in turn leads to higher dipole strength thereby affecting the overall cell capacitance. Variation of specific capacitance as a function of scan rate and number of printing passes is shown in Fig. 3d. The highest specific capacitance (110 mF g\(^{-1}\)) was for a 35 printing pass device at a scan rate of 10 mV s\(^{-1}\). Despite the linearity displayed in Fig. 3b, printing involving more than 35 passes was not pursued as printing conditions became more difficult as the amount of protein loading increased due to air turbulence between nozzle tip and substrate surface, reducing the overall print quality and resolution [50].

Standard MCs displayed a symmetric galvanostatic charge-discharge (GCD) profile at current densities between 0.013 and 0.08 mA cm\(^{-2}\) (Fig. 4a), indicating excellent electrochemical reaction kinetics. Notably, the voltage drop as current flowed (IR drop) was also very small. For example, the GCD curve at 0.06 mA cm\(^{-2}\) showed an IR drop of only 0.052 V, indicating an excellent electrochemical performance [66, 67]. Charge-discharge stability was examined for a standard MC at a constant current density of 0.06 mA cm\(^{-2}\). Even after 10,000 cycles it demonstrated excellent electrochemical stability with 91% retention of its initial performance (Figure 4b; profiles for last six cycles are plotted in the inset). The energy/coulombic efficiency (\( \eta \)) of the MC, a parameter crucial for determining cycle stability [36], was determined from the ratio of discharging time (\( t_d \)) and charging time (\( t_c \)) when the charge–discharge current densities were equal, according to: \( \eta = \frac{t_d}{t_c} \times 100\% \). The average coulombic efficiency was found to be 96% for standard MCs. It has been previously discovered by Dr. Tan’s lab, that charge transport in protein multilayers devoid of an electrolyte occurs through charge hopping between adjacent protein layers which is diffusion dependant thereby resulting in prolonged discharge times compared to electrolyte aided systems [40]. In the manuscript, direct evidence for charge storage capacity within RC-LH1 complexes/multilayers was demonstrated using Kelvin-probe and scanning-capacitance microscopy (KPFM). KPFM successfully suggested the charge trapping in a capacitor that not only harvests incoming light and segregates charges but also stores them. Power density (P), how quickly a capacitor can be charged, and energy density (E), how much energy can be stored [68], were determined from GCD curves at different current densities. A Ragone plot of energy density versus power density for a standard MC is plotted in Fig. 4b. The energy density and power density were calculated using formulae \( E = 0.5 CV \) [2] and \( P = E/t \), where \( t \) is the discharge time, respectively [68]. The standard MC displayed an energy density of between 5.0 and 4.1 mWh kg\(^{-1}\) over a power density range of 6.5 to 40 mW kg\(^{-1}\).

To explore the customisability of the device, three identical standard MCs were connected either in series or in parallel. Compared to a single MC (potential window: 1 V, discharge time: 50 s), the three MCs connected in series exhibited a three-fold increase in charge–discharge
Fig. 4. Device performance and Storage of externally injected charges. a) GCD profiles for a standard MC at different current densities. b) Ragone plot for a standard MC and percentage retention of capacitance at a current density of 0.063 mA g\(^{-1}\) by a standard MC as a function of charge/discharge cycle number. Inset shows the GCD profiles for the last six charge/discharge cycles. c) Galvanostatic charge/discharge profiles collected at a current density of 0.063 mA g\(^{-1}\) for a single standard MC and for three connected in series or in parallel. d) Three MCs in series were connected to the sourcemeter (left image). LCD watch was connected to complete the circuit and external charges were injected for 15 mins by applying a constant current of 10 µA (middle image). The sourcemeter was switched off and charged MCs powered an LCD watch for approximately 1–2 s (right image). Insets shows the zoomed in images of the LCD Digital watch. e) Schematic illustration demonstrating the standard MC based on bacterial light energy harvesting apparatuses.
voltage window (3 V) with almost the same discharge time (Fig. 4c, red) and the three MCs connected in parallel presented a three-fold increase in the discharge time (150 s) with 1 V voltage window (Fig. 4c, blue). This demonstrated simple manipulation of voltage and capacitance by merely designing the print pattern. Finally, three MCs were connected in series and were charged by applying a constant current of 10 µA for 15 mins. This provided sufficient charge to power up a low energy consumption LCD display watch for approximately 1–2 s (Fig. 4d, e).

Use of a PET film as the non-conducting substrate enabled the printing of a potentially flexible micro-capacitor (Fig. 5a). To evaluate feasibility, standard MCs were subjected to repeated deformation to a defined angle in a test rig (Figure S7 in Supplementary Information) and their electrochemical properties were tested. Bending to angles up to 180° had no significant effect on device CV profile (Fig. 5b) indicating preservation of structural integrity and the capacitive behaviour of the device. Calculated specific capacitance was unaffected except at the largest bending angle where a ~5% drop was seen (Fig. 5c). Similarly, GCD measurements also showed that bending had no significant effect on device performance (Figure S8 in Supplementary Information). This excellent stability extended over multiple deformations, with a 93% retention of specific capacitance obtained after 1000 bending cycles with a 135° bending angle (Fig. 5c).

4. Conclusions

In this work, we have demonstrated an all printed, solid state, flexible Photo-electro protein micro-capacitor that can utilize the low light intensities typically found in indoor settings. To achieve this, we have used as the photovoltaic component a natural photosynthetic protein that has evolved to convert low intensity solar energy with high quantum efficiency, having an architecture that surrounds the photovoltaic module (RC) with a highly quantum efficient solar energy collecting module (LH1). After optimisation, printed biohybrid micro-capacitors achieved a specific capacitance of 110 mF/g at a scan rate of 10 mV/s. The micro-capacitors had an output sufficient to power a nano/micro electronic device, delivering an energy density of 5 Wh kg⁻¹ at a power density of 6.5 mW kg⁻¹ and 4.1 mW kg⁻¹ at a power density of 40 mW kg⁻¹. The specific capacitance is proportional to photosynthetic efficiency; and are dependent on the wavelength of light absorbed by the protein complexes. The biggest disadvantage of photosynthetic protein-based devices is that their performance is limited by slow diffusion processes rather than the ability of proteins to absorb light energy and separate charge. The efficiencies are also restricted by the laws of thermodynamics i.e., there is a theoretical limit to the highest achievable efficiency. In real scenario, these photosynthetic bacteria don’t use all incoming light (due to respiration, reflection, light inhibition and light saturation) which reduces the overall photosynthetic efficiency to be between 3%–6% based on total solar radiation. On top of this, the incident light intensity used in our work was only 0.002 Sun (indoor setting light), which further reduces the generation of photoactive charges. In this case, different approaches could be used to expand the output of these micro-capacitors, but there are practical limitations. We tried using higher concentrations of RC-LH1 to improve reaction flux and light harvesting but the solution was already highly concentrated and, by its nature, highly viscous and challenging to form a cone-jet ink. Also, depending on the configuration of a device, adding more protein by increasing thickness or concentration can produce diminishing returns due to self-shading, increased diffusion lengths and so on. So, increasing the concentration or thickness of patterns did not necessarily increase the capacitance and pose additional technical challenges. However, there is still lot of room to further optimize the performance of these micro-capacitors through design optimization. It has been found that several light trapping structures like metal nanoparticles, surface plasmons, photonic crystals, Johnson solid reflectors, light couplers have a great potential in the enhancement of the optical absorption and conversion efficiency across a wide wavelength range, as does the addition of synthetic and or natural accessory light harvesting pigments.

The EHD printed devices were operationally and mechanically robust retaining 91% of their initial capacitance after 10,000 charging/discharging cycles and 93% of their initial capacitance after 1000 bending cycles. We connected three micro-capacitor units in both series and parallel for efficient power source. The data demonstrate that such printed flexible micro-capacitor have a promising future as flexible energy-storage modules for robotics and wearable electronic devices. Additionally, the work provides new insights into the development of solid state Photo-electro micro-capacitors based on bio sustainable and environmentally benign photosynthetic proteins.

CRediT authorship contribution statement

Nikita Paul: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing. Lakshmi Suresh: Conceptualization, Investigation, Data curation, Formal analysis. Jaemin Seo: Visualization, Data curation, Formal analysis. Yaoxin Zhang: Visualization. Hangbo Zhao: Data curation, Formal analysis, Investigation, Writing – review & editing. Michael R. Jones: Funding acquisition, Validation, Writing – review & editing. Swee Ching Tan: Conceptualization, Validation, Supervision, Funding acquisition, Project administration.
Declaration of Competing Interest

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Data availability

Data will be made available on request.

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Supplementary materials


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