Powering a Microprocessor by Photosynthesis

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30 Abstract

Sustainable, affordable and decentralised sources of electrical energy are required to power the network of electronic devices known as the Internet of Things. Power consumption for a single Internet of Things device is modest, ranging from uW to mW, but the number of Internet of Things devices has already reached many billions and is expected to grow to one trillion by 2035, requiring a vast number of portable energy sources (e.g., a battery or an energy harvester). Batteries rely largely on expensive and unsustainable materials (e.g., rare earth elements) and their charge eventually runs out. Existing energy harvesters (e.g., solar, temperature, vibration) are longer lasting but may have adverse effects on the environment (e.g., hazardous materials are used in the production of photovoltaics).

Here, we describe a bio-photovoltaic energy harvester system using photosynthetic microorganisms on an aluminium anode that can power an Arm Cortex M0+, a microprocessor widely used in Internet of Things applications. The proposed energy harvester has operated the Arm Cortex M0+ for over six months in a domestic environment under natural light. It is comparable in size to an AA battery, and is built using common, durable, inexpensive and largely recyclable materials.

61 Introduction

62 The Internet of Things (IoT) comprises a vast network of small computational devices deployed 63 in domestic, commercial, industrial and natural environments, connected to a myriad of "things" 64 for sensing and transmitting their status, responding and communicating accordingly. This network 65 has revolutionised many aspects of the modern world and will transform information exchange in smart homes, cities, factories, farms and natural environments¹⁻³. The IoT is growing rapidly. With 66 several billion IoT devices already in existence⁴, it is expected to reach one trillion by 2035⁵. Many 67 68 IoT devices consume power in the range of µW to mW, and are frequently powered by a battery. 69 However, powering one trillion IoT devices by lithium-ion batteries, would require 109,000 tonnes 70 of lithium, three times more than the world's annual production in 2017⁶, and not sustainable. 71 Other battery types would also require major use of natural resources, or routine recharging and 72 eventual replacement with inevitable negative environmental impact^{7,8}. Consequently, energy 73 harvesting - rather than energy storage - is desirable for powering IoT devices⁹. The ideal energy 74 harvesting system must deliver sufficient power for continuous sensing¹⁰, and should be built using 75 inexpensive and common materials, avoiding toxic components.

76 To date, examples of energy harvesting systems for IoT devices include photovoltaics $(PV)^{11}$, microbial fuel cells (MFC)¹², and other micro-scale energy harvesting materials¹³. PV are arguably 77 the most studied, developed and perhaps most immediately practicable¹⁴. However, they do not 78 79 provide power during dark periods. Microbial fuel cells (MFCs) use bacteria to oxidize a chemical fuel and generate electrical energy¹⁵. Although they can operate in the dark, MFCs depend on the 80 metabolism of heterotrophic bacteria and require a supply of organic matter¹⁶. Photosynthetic 81 82 microorganisms can be used instead of heterotrophic bacteria in the anodic chamber of these biological fuel cells. Such devices are often referred to as biophotovoltaics (BPV) as the electric 83 84 current is ultimately based on electrons liberated from water through photosynthetic photolysis of 85 water¹⁷⁻¹⁹. This removes the need to supply the device with organic matter as chemical fuel, and uses solar energy to drive it. One of the key components in BPV devices is the anode, which 86 87 channels the current generated by the microorganisms into an external circuit. The ideal anode 88 must be biocompatible, with adequate electric conductivity and optical properties to permit current 89 flow and light diffusion. For BPV devices to be implemented at large scale, the anode should be 90 durable and use abundant and low-cost materials²⁰⁻²¹.

91 Here, we report the development of a novel aluminium-anode bio-photo-voltaic system (Al-BPV) 92 with as photo-active component the commonly used model photosynthetic bacterium 93 Synechocystis sp. PCC6803 (hereafter referred to as Synechocystis). The system was built in a 94 small form factor (*i.e.*, small size) using common, durable, and recyclable materials. The system 95 successfully and continuously powered for over six months a microprocessor based on an Arm 96 Cortex M0+ central processing unit (CPU), one of the most commonly used CPUs found already 97 in many commercial IoT applications. The test was conducted in a domestic environment without 98 any dedicated artificial lighting system, additional battery or organic fuel supplement. The 99 mechanism of operation of the Al-BPV system was studied using electrochemistry (cyclic 100 voltammetry, potentiodynamic sweep and electrochemical impedance spectroscopy), microscopy, 101 and microbiological characterisation.

102 This study demonstrates the robustness and practicability of an Al-BPV as a durable and reliable 103 source of renewable power for untethered applications, paving the way for the large-scale 104 implementation of photosynthetically powered micro-electronics.

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107 **Results and Discussion**

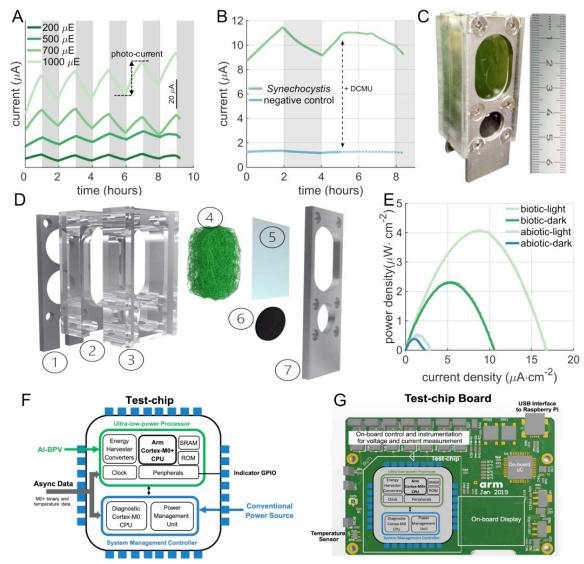
108 *Rationale for using aluminium as anode*

109 To select an optimal anodic material to be used in photosynthetically driven electrochemical 110 systems, aluminium was considered because it is one of the most abundant metals in the Earth's 111 crust, available in large quantity as waste in the environment, and classified as not toxic²². The use 112 of an aluminium anode in electrical energy generation systems has been described before, in 113 aluminium-air batteries (AAB)²³. In these, electrochemical aluminium oxidation in an alkaline 114 medium is combined with oxygen reduction at the cathode. To our knowledge, the effect of introducing biological components into AAB has not been studied. Several studies have examined 115 116 the physiological effects of aluminium on plants, cyanobacteria and microalgae, with results 117 depending on the organism considered²⁴⁻²⁵. We tested growth of Synechocystis cultures in the 118 presence of metallic aluminium, and found that they reached a cell density similar to control 119 samples without aluminium (Fig.S1), suggesting that aluminium is biocompatible with 120 Svnechocvstis.

122 *Light-dependent power production from a prototype Al-BPV*

123 We built a prototype BPV system (Al-BPV) using aluminium wool as anode (Fig.S2), with a 124 commercial open-air cathode, stainless steel electric connectors and plastic vessels (Fig.S3). The 125 prototype Al-BPV system was inoculated with Synechocystis (Fig.S4A), and first tested in a 126 laboratory-controlled environment. The system gave peak power density of 0.2 uW cm⁻² and 0.37 μ W cm⁻² under dark and light conditions respectively, indicating a photoactive component to 127 power production. These figures were significantly greater than those observed in an abiotic 128 129 negative control (Fig.S4B). The effect of illumination on the electrical output observed here in the 130 prototype Al-BPV system is not seen in AABs, which are not photo-active when illuminated with 131 visible light²⁶, although in AABs a modest increase in the power output in response to light might be observed because of the thermal effect of illumination²⁷. Thus, the presence of a much bigger 132 133 photo-effect in the presence of Synechocystis compared to the abiotic control (Fig.S4B), and the 134 large increase in amplitude in response to increased light intensity (Fig.1A) indicate that current 135 production depends on the photo-active component of the system, (i.e., the photosynthetic 136 microorganisms). The effect of adding the photosynthesis inhibitor 3-(3,4-dichlorophenyl)-1,1dimethylurea (DCMU)²⁸ to the anodic chamber was tested. DCMU addition had an immediate 137 effect on photo-current (Fig.1B), which stopped increasing and then decreased. The effect of 138 139 inactivating the photosynthetic microorganisms was tested by autoclaving the inoculated anode. 140 This abolished autofluorescence, indicating loss of photosynthetic activity, and resulted in almost 141 complete loss of light-dependent current (Fig. S5). These observations indicate that current 142 production from the Al-BPV depends on the biological activity of the microorganisms.

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150 Fig. 1. Development and characterisation of the prototype and compact Al-BPV systems, and 151 diagrams of the Arm Cortex-M0+ processor in a test-chip and board. A) Chronoamperometry 152 for the prototype Al-BPV system under 2 hours dark/light cycles. Effect of increasing light inten-153 sities on the photo-current. B) Effect on photocurrent for the prototype Al-BPV system of addition 154 of the photosynthetic inhibitor DCMU (35 µM), including for the abiotic negative control with 155 BG11 medium only (blue). C) Photograph of the compact Al-BPV system. D) 3D exploded dia-156 gram of the compact Al-BPV system. The diagram shows two stainless steel metal plates (1 and 157 7), an acrylic compartment made of two parts (2,3), an aluminium anode colonised with photosyn-158 thetic microorganisms (4), a Teflon gas-permeable membrane (5) and an open air cathode (6). 159 Stainless-steel screws are not shown in this diagram. E) Power curve for the compact Al-BPV 160 system and abiotic negative control (BG11 only) (scans at rate of 0.1 mV s⁻¹). F,G) Schematic diagrams of the test-chip and its board. The test-chip includes two blocks: an ultra-low-power 161 162 processor consisting of an Arm Cortex-M0+ CPU, SRAM, ROM, clock, peripherals, and energy 163 harvesting converters, and a system management controller consisting of a diagnostic Arm Cortex-

164 M0 CPU and a power management unit. The Al-BPV powers the ultra-low-power processor whilst 165 the system management controller is powered by a USB power source. The test-chip board con-166 tains the test-chip, a temperature sensor, voltage and current measurement circuitry, a microcon-167 troller taking the voltage, current and temperature measurements, a display and a USB interface to 168 an external Raspberry Pi. The Arm Cortex-M0+ requires a minimum of 0.3 μ W (at 0.3V) to run 169 its computational work at a frequency of 10 kHz. The minimum power consumption drops to 0.24 170 µW during the standby mode when computations are not running. The system management con-171 troller in the test-chip was powered by a conventional USB power source.

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174 Developing a compact Al-BPV for powering the Arm Cortex-M0+ in a domestic environment

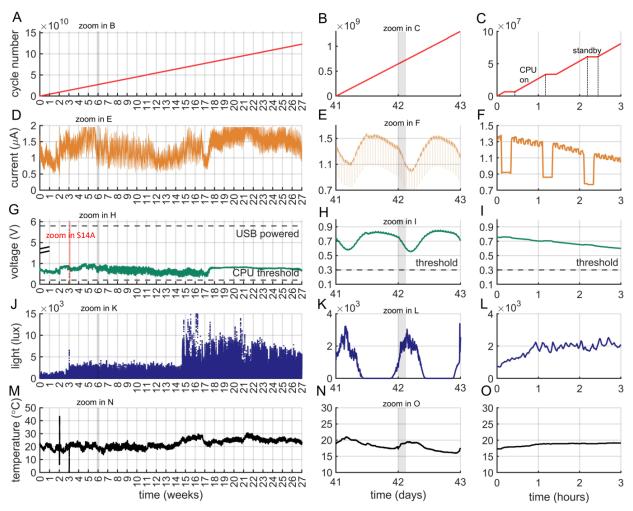
Having demonstrated the possibility of power generation in an Al-BPV system, we constructed a 175 176 compact version with a small form factor, similar in size to an AA battery, referred to as the 177 compact Al-BPV (Fig.1C-E and Fig.S6,7). Characterisation in a controlled laboratory environment (Fig.S8) showed a peak power density of 4.2 µW cm⁻² and an output maintained for 178 179 over 20 days. This should be sufficient to power a real-world device, such as the Arm Cortex-M0+ 180 CPU²⁹. This is a programmable 32-bit RISC microprocessor, highly energy- and area-efficient, supporting the ARMv6-M Thumb instruction set (Fig.1F). The Arm Cortex-M0+ is used in many 181 182 microcontrollers and embedded applications that can run programs written in high-level programming languages. In the experiments, we used a test-chip designed and implemented by 183 Arm³⁰⁻³¹ comprising the Arm Cortex-M0+ and a system management controller (Fig.1G). 184

We programmed the Cortex-M0+ CPU to calculate a sum of consecutive integers (S_n) as an example compute workload, and assess the correctness of the computation by verifying the sum against a precomputed value ($S_n = \frac{n(a_1 + a_n)}{2}$). We programmed the CPU to perform 45 minutes of computation work followed by 15 minutes of standby (Fig.S9).

The test was conducted over half a year in a domestic setting in Cambridge (UK), with ambient light as the energy input (**Fig.S10**). The anode-to-cathode voltage, current, ambient temperature and light were measured by the electronics built in the test-chip board and then recorded and visualised on the cloud-based platform ThingSpeakTM via a Raspberry-pi/router (**Figures 2 and S11**). During the test, the Arm Cortex-M0+ processor performed a total of 1.23E+11 cycles, resulting in a linear and continuous increase in the number of calculations performed over time (**Fig.2A-C**). Throughout the test, the Arm Cortex-M0+ processor drew an average current from 196 the compact Al-BPV of $1.4\pm0.4 \ \mu$ A with a voltage of $0.72\pm0.14 \ V$ (**Fig.2D-I**). The light profile 197 displayed the expected diurnal cycle (**Fig. 2J-L**) with ambient temperature ranging from a 198 minimum of 13.8 °C to a max of 30.7 °C (**Fig. 2M-O**). As the average power drawn from the 199 compact Al-BPV during the 27 weeks of experimental run ($1.05 \ \mu$ W) was larger than the minimum 200 power required to run the CPU (i.e., $0.3 \ \mu$ W), it is likely that a smaller power-generating system 201 could be used, or that more computationally intensive algorithms could be performed.

202 The system was set up so that if the CPU failed, e.g., the compact Al-BPV cannot supply minimum 203 operating power, the processor would automatically be switched to the mains electricity (USB 204 powered). This would be displayed by recording a voltage >5V, and the system would need to be 205 reset. To test this, we deliberately induced failure (for about 90 minutes at the end of the third 206 week) by positioning an ice-pack near the temperature probe mounted on the test-chip which 207 caused a localised lowering of the ambient temperature below 5 °C (Fig.2M red background), 208 which is much below the minimum operating temperature 13.8 °C, without varying the 209 temperature experienced by the compact Al-BPV. In this instance, the software controlling the 210 operation of the CPU triggered to switch the power of the CPU from the Al-BPV to the USB power 211 supply. Apart from this instance, switching to >5V was not observed at any other time during the 212 experiment shown in Figure 2, indicating that the CPU was powered successfully throughout by 213 the Al-BPV. The system also incorporated an LED that flashed when the CPU was powered by 214 the Al-BPV. Failure of the Al-BPV to power the CPU would cause the LED to stop flashing until 215 the system was reset. Failure was not seen at any time during the experimental run except when 216 deliberately induced.

217 The current and voltage profile recorded during the six months of testing (Fig.2D-G) did not show 218 consistent decline by the end of the test, and the system was still running on the date of submission 219 of this manuscript (2022/01/19 - see Channel 1033008 (https://thingspeak.com/channels/1033008) 220 of the ThingSpeakTM platform (Fig.S11)). The durability of the compact Al-BPV system was also 221 demonstrated in a parallel experimental test run for more than four months (Fig.S12). This test 222 was stopped for analysis of the anode and anodic microbiome (see below). A larger prototype has 223 remained functional for over two years (Fig.S13). To our knowledge, this study is the first to report 224 continuous powering of a microprocessor using a bio-electrochemical system driven by 225 photosynthetic microorganisms with ambient light as the sole energy input, without the need for 226 any additional battery, or organic fuel and outside of laboratory-controlled conditions.



229 Fig. 2. Powering the Arm Cortex-M0+ processor by the compact Al-BPV system in a 230 domestic environment (from 2021/02/20 to 2021/08/02). The CPU alternated in cycles of 45 minutes of computing mode and 15 minutes of standby. The data presented in the left column 231 232 (A,D,G,J and M) show the entire experimental run. Central columns (B,E,H,K and N) illustrate 233 insets of two days of recording taken from an arbitrary point (depicted by the gray-shaded regions) 234 of the left column. The data presented in the right column (C,F,I,L and O) show three hours of 235 recording taken from an arbitrary point (depicted by the grey-shaded regions) of the central 236 column. A-C) Cumulative number of cycles of the sum of consecutive integers computed by the 237 CPU. D-F) Electrical current generated by the BPV device. G-I) Absolute potential difference between the anode and cathode of the BPV device. The dotted line indicates the threshold of 238 239 electric potential below which the processor cannot be powered. J-L) Ambient light measured by 240 a light sensor placed in proximity to the Al-BPV system. M-O) Environmental temperature measured by a temperature sensor integrated into the test-chip board. The red-shaded regions 241 242 depicted in panels G and M indicate a phase during which the Al-BPV failed to power the CPU 243 induced by deliberately lowering the ambient temperature below 5 C°, as zoomed in Fig.S14).

Working hypothesis for the mechanism of operation of the Al-BPV system

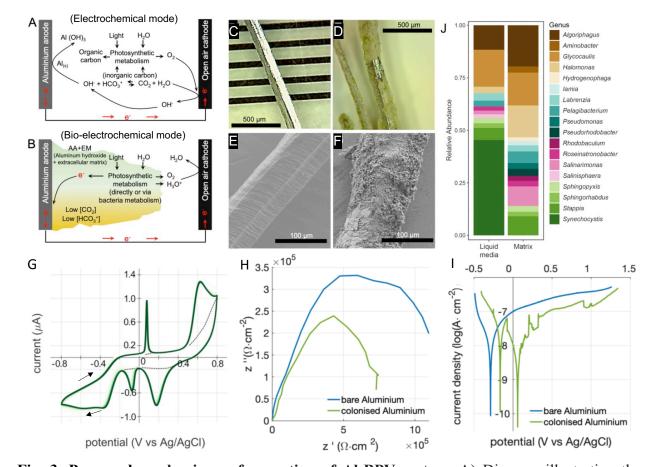
246 There are two possible modes of operation for the Al-BPV, which we refer to for simplicity as 247 'electrochemical' and 'bio-electrochemical' modes. Although both rely on the photosynthetic 248 activity of the microorganisms in the anodic chamber, in the electrochemical mode, the 249 photosynthetic microorganisms do not directly generate current responsible for the electrical 250 output. Instead, they provide a favourable environment for aluminium oxidation, e.g., through 251 local alkalinization, and electrical output stems from current derived from electrochemical 252 aluminium oxidation. In this electrochemical mode the Al-BPV system works as a photosynthetic 253 microbially assisted aluminium air battery (Fig.3A). By contrast, in the bio-electrochemical mode, 254 the photosynthetic microorganisms themselves generate the electrons constituting the electrical 255 output of the Al-BPV system. Electron transfer would presumably occur via the outer bacterial 256 membranes through the extracellular matrix to the aluminium, perhaps involving secreted electron 257 shuttles³² (Fig.3B). It is possible that both modes coexist and the predominant mode changes over 258 time.

259 A number of analyses were carried out to assess the importance of the two modes. Optical 260 microscopy and scanning electronic microscopy (SEM) of filaments of aluminium taken from a 261 device that had operated for four months showed a dense layer of material had built up on the 262 anode, possibly including oxidation products and biofilm components (Fig.3C-F, S15). This layer, 263 accumulated over time, would be expected to limit further aluminium oxidation. We also carried 264 out cyclic voltammetry (CV) analysis on aluminium hydroxide and extracellular matrix scraped 265 from the anode of a mature Al-BPV system. CVs showed oxidation and reduction peaks indicating 266 the presence of one or more redox active species (Fig.3G), which could most readily be explained 267 if they were generated by microorganisms at the anode. Electrochemical impedance spectroscopy 268 (EIS) measurements showed that the Rp of a bare Al anode was approximately two-fold greater 269 than that of the anode taken from an Al-BPV system four months old (Fig.3H). However, a 270 potentiodynamic sweep (PDS) curve (Fig.3I) of new aluminium filaments without biofilms 271 submerged in BG11 medium showed only a weak increase of current with potential in the anodic 272 branch (the region with potential increasing from ca. -0.3 V), thus excluding pitting (i.e., fast 273 dissolution of aluminium). The PDS curve of the colonised aluminium (Fig. 3I) also did not show 274 a strong current increase in the anodic branch. From these measurements, there is no indication that anodic polarisation would lead to fast corrosion of the aluminium surface in new or colonised 275

filaments, consistent with the fact that although microbially influenced corrosion is known to affect iron, it is much less common on aluminium³³. Although bacteria are known to affect aluminium alloys in chloride-rich environments (*i.e.*, seawater)^{34,35}, the mineral medium used in our study had a low chloride concentration (~0.5 mM), making microbial corrosion less likely.

280 In summary, the amount of material deposited on the anode increased with time, and the 281 polarization resistance decreased with time. The PDS data indicate that fast corrosion of the 282 aluminium was not occurring. The decrease of the polarisation resistance may indicate 283 modification of the aluminium oxide layer by the microorganisms, facilitating electron transfer 284 through the usually insulating oxide. The persistent current output and photo-response seen in Al-285 BPV systems several months old even when the anode was covered with passivating components 286 suggest the bio-electrochemical mode makes an important contribution to electrical output with 287 mature systems. A mixed, dynamic scenario, with a change in the relative importance of the two 288 modes could explain the variation of current output observed during the long-term operation of the 289 Al-BPV (e.g., Fig2.D,G and Fig.S12D,G). The electrical connection of the microorganisms to the 290 electrode would presumably depend on factors such as their adhesion, the build-up of material on 291 the electrode, and the production of redox mediators by the microorganisms. These properties 292 would affect the performance of the device as an energy harvester. For future applications, 293 microorganisms could be selected to optimize the relevant properties.

294 We also sequenced prokaryotic ribosomal RNA genes from DNA extracted from cells in a 295 compact-Al-BPV system that had initially been inoculated with cells of the cyanobacterium 296 Synechocystis, but then operated for several months in a non-sterile domestic environment. 297 Evidence was found for a complex biome containing a wide range of microorganisms, including 298 representatives of Halomonas and Pseudomonas (Fig.3J), genera which include electroactive 299 bacteria³⁶⁻³⁷. These microbes might provide redox active electron shuttles (which many electroactive bacteria are known to do³⁸), and/or oxidise organic metabolites received from the 300 301 photoautotrophs, transferring electrons to the anode (Fig.S16). Having a consortium of 302 microorganisms in the anode compartment, with photoautotrophs and heterotrophs sharing 303 different functions, may offer enhanced stability and less susceptibility to contamination³⁹⁻⁴⁰. The 304 change in current output seen over time in long-running experiments (e.g., Fig.2D) might reflect 305 a change in microbial composition.



308 Fig. 3. Proposed mechanisms of operation of Al-BPV system. A) Diagram illustrating the 309 processes during the proposed electrochemical operational mode. B) Diagram illustrating the 310 processes during the proposed bio-electrochemical operational mode. C,D) Optical microscopy of 311 new (C) and colonised aluminium anodes (D). E,F) Electron microscopy of new (E) and colonised 312 aluminium anodes (F).G) Cyclic voltammetry performed on a sample of aluminium hydroxide and 313 extracellular components scraped from an aluminium anode taken from an Al-BPV system several months old (21 scans at rate of 10 mV s⁻¹, Screen-Printed Gold Electrode C223BT. H) 314 315 Electrochemical impedance spectroscopy on a bare aluminium anode in BG11 growth medium 316 without microbes (blue trace) and a colonised aluminium anode (green trace). The diameter of the semi-circle in the plot corresponds approximately to the polarization resistance Rp. I) 317 Potentiodynamic sweep on bare aluminium anode submerged in BG11 growth medium without 318 319 microbes (blue trace) and colonised aluminium anode (green trace). J) Identification by ribosomal 320 RNA sequencing of the prokaryotic microbiome found in the liquid phase and matrix (aluminium 321 hydroxide and extracellular components). Sample was taken from an Al-BPV system after four 322 months of operation in a domestic environment.

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326 *Conclusion*

- We have developed a novel aluminium-anode biophotovoltaic system (Al-BPV) based on widespread non-toxic photosynthetic microorganisms (*Synechocystis*) built using common, durable, inexpensive and largely recyclable materials (**Fig.1C-D**, **S2**, **S6-S7**).
- The compact Al-BPV is comparable in size to an AA battery, and it is capable of powering the Arm Cortex M0+ processor (**Fig.1F,G** and **Fig.S11**) for more than six months in a domestic environment without any subsidiary energy storage device, artificial lighting or organic feeding (**Fig.2**).
- We propose the Al-BPV system as a practical alternative to PVs and MFCs for powering small electronic devices for numerous domestic, industrial and agricultural applications, and potentially in remote locations. Our system has a unique place in the landscape of this technology (**Fig.S17**, **Table S1**) and paves the way for the development and implementation of a vast number of photosynthetically-powered IoT devices.
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- Biotechnology and Biological Sciences Research Council studentship, BB/M011194/1 (to ASc),
- 496 National Biofilms Innovation Consortium 02POC19029 (to SJLR)
- The Italian Ministry of University and Research (MIUR), within the SIR2014 Grant, project
 RBSI14JKU3 (to PB).
- 499 Natural Environment Research Council National Capability Science & Facilities funding
- 500 NE/R017050/1 and Scottish Association for Marine Science internal research funds (to DHG).
- 501

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- 512

513 *Competing interests*

- 514 CJH and PB hold Patent GB2466415 Hydrogen and electrical current production from 515 photosynthetically driven semibiological devices.
- 516

517 Data and materials availability

- 518 The data that support the plots within this paper and other findings of this study are available at: 519 <u>https://doi.org/10.17863/CAM.74822</u>
- 520 Supplementary Materials:
- 521 Figs. S1 to S17
- 522 Tables S1
- 523 Materials and Methods