Journal of Science: Advanced Materials and Devices 9 (2024) 100674

Contents lists available at ScienceDirect

Journal of Science: Advanced Materials and Devices

journal homepage: www.elsevier.com/locate/jsamd

Sustainable power generation from live freshwater photosynthetic filamentous macroalgae *Pithophora*

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ARTICLE INFO

Keywords:
Photosynthesis
Macroalgae
Microalgae
Biophotovoltaics
Exoelectrogenesis Internet of things

ABSTRACT

Photosynthesis is the natural eternal process of conversion of solar energy into Chemical energy by living chlorophyllous organisms. The direct conversion of sunlight into electrical current by using photosynthetic organisms has the potential to produce green energy. Conventional bio-photovoltaic cells have utilized unicellular photosynthetic microorganisms such as cyanobacteria and unicellular green algae. This study describes electricity generation through a quasi-solid-state device by utilizing live freshwater macroalgae. Here, we fabricated a simple bio-photovoltaic device with filamentous macroalgae *Pithophora roettleri* as photoactive materials. The filamentous alga *Pithophora* belonging to the family of green algae, is generally found growing at the bottom or forming dense mats on the surface of aquatic habitats. The algae were collected from a pond located in the neighbourhood and fabricated a device by sandwiching the algal biofilm between activated carbon-coated copper (Cu) and titanium oxide (TiO2) coated fluorine-doped tin oxide (FTO) coated glass slide. The fabricated optimized device has exhibited a considerable amount of photo-generated current and photo-generated voltage generation under the white light and UV light irradiation The optimized device (with 1 cm^2 area) exhibits 10.19 μA short circuit photocurrent and 0.35 V open circuit photovoltage in white light (100 mW/cm^2) irradiance and exhibits 1.25 mA photocurrent and 0.5 V photovoltage in UV light (365 nm LED with 20 mW/cm^2 intensity). To understand applicability, 10 devices were connected in a series that delivered 5.53 V in outdoors under natural sunlight with 0.6 Sun intensity.

1. Introduction

Today it is well accepted that humanity is facing severe challenges due to decreasing fossil fuel reserves and increasing energy demand for huge population growth and unsustainable lifestyle choices. Even if proposed energy policies can be efficiently adapted globally, the demand for energy by 2040 would grow by 32 % (vs. 2013) to reach 17,934 million tons of oil equivalent. It is very clear that to overcome this energy demand, it would require a minimum 15 % energy production increment, which will lead to an increase in CO_2 emissions even further. To reduce dependency on fossil fuel and carbon footprint we need alternative, renewable and green energy sources. Nowadays, solar power is considered an attractive source of renewable energy, as, on average, the Earth receives way more energy from the sun in a given time than is required for human consumption.

Solar energy harvesting has emerged as a promising method for generating electricity, and the design of solar cells has undergone various modifications to improve their efficiency in converting sunlight into usable energy. Silicon-based solar cells are commonly used, but there is a growing interest in developing solar cells that utilize non-toxic and renewable materials to avoid any negative impact on the environment. Current photosynthetic solar cells often make use of non-

Peer review under responsibility of Vietnam National University, Hanoi.
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https://doi.org/10.1016/j.jsamd.2024.100674
Received 5 October 2023; Received in revised form 7 January 2024; Accepted 17 January 2024
Available online 26 January 2024

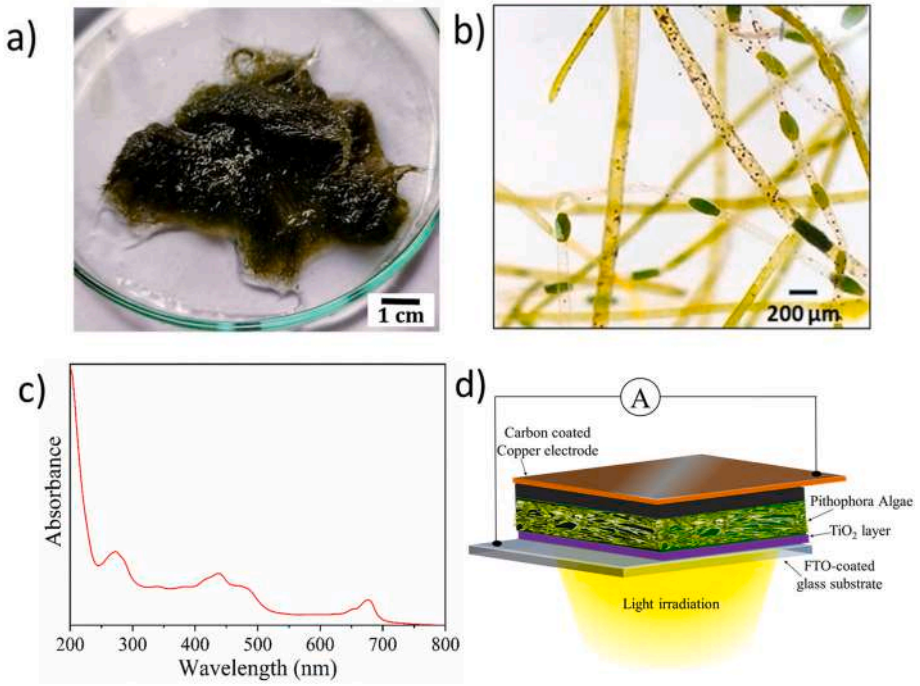

Fig. 1. a) The camera image of the as collected algae; b) Microscopic image of the algae; c) UV–Vis spectrum of the algae; d) Schematic diagram of the device.

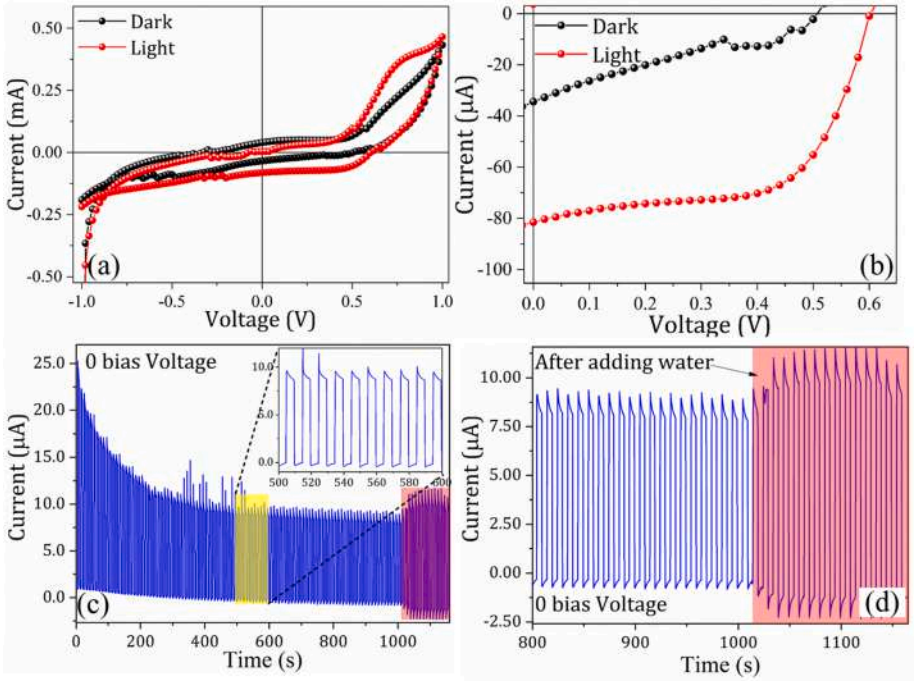

Fig. 2. a) I–V characteristic, b) Maximized view of the I-V, c) Time-dependent photocurrent (I-t), and d) maximized view of I-t for the device FTO/TiO_2/Pithophora/Carbon under 100 mW/cm^2 incident light power.

renewable components, which can pose environmental risks [1]. Therefore, there is a need to develop renewable and non-toxic photosynthetic solar cells that can efficiently produce electricity while minimizing their impact on the environment. In the past few years, in addition to inorganic photovoltaic devices, bio photovoltaics (BPVs, also known as biological solar cells) have emerged as an environmental friendly and low-cost approach to harvesting solar energy and directly converting solar energy into electrical power. These kinds of bio solar cells utilize the photosynthetic properties of living cells, such as cyanobacteria, algae, etc., to convert light energy into electric current that can be used to provide electricity.

Bio-photovoltaics (BPV) is a comparatively new research thrust in bioelectricity production from biomaterials. The working principle of BPV cells is the direct conversion of light energy into electrical energy using green algae or cyanobacteria. Photosynthetic organisms will use their Photosystem II and Photosystem I present in the thylakoid and sunlight to split the water molecule by the process called Hill reaction. Live algal cells are extracting electrons by photolysis of water catalyzed

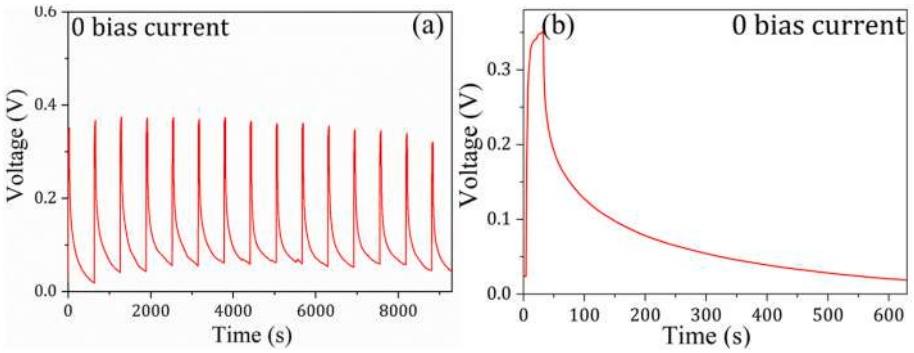

Fig. 3. a) Time-dependent photovoltage (V-t) and b) maximized view of one pulse in V-t graph for the device FTO/TiO_2/Pithophora/Carbon under 100 mW/cm^2 incident light power.

Table 1
Comparison of performance of different biophotovoltaics devices.

Photosynthetic organism	Device structure	Open circuit voltage	Photocurrent density mA/cm^2	References
Nostoc sp. ATCC 27893	Three electrode PEC with anode of CNT/Carbon Paper and cathode of Laccase/CNT/ Carbon Paper electrode		0.024	[25]
Paulschulzia pseudovolvox	Three electrode PEC with mediator with graphite electrode		0.0115	[26]
Chlorella vulgaris	Three-electrode PEC with anode of TiO_2/rGO/carbon cloth and cathode of carbon cloth electrode	0.127V	0.0654	[27]
Mixed culture of algae and cyanobacteria	Three electrode PEC with graphite electrode		0.00118	[28]
Leptolyngbia sp.	Three electrode PEC with Au nanoparticle decorated graphite electrode		0.0063	[29]
Gloeocapsopsis sp. UTEXB3054	Three electrode PEC with graphite electrode		0.00226	[30]
Synechococcus sp.	Two chambered biophotovoltaic device with Pt mesh and Carbon nanofluid.		~0.014	[31]
Chlorella vulgaris	Three electrode PEC with modified Au electrode		0.01366	[32]
Pithophora roettleri	Two electrode mediator free sandwich device with TiO_2 coated FTO glass and Activated carbon coated Cu electrode	~0.58V	1.25	This work.

by photosystem II (PS II). These electrons are then transferred by the photosynthetic electron transport chain (PETC) and produce NADPH. During this process, it will create a gradient potential to produce ATP, at the same time, some of the electrons are derived from the electron transport chain and enter to cytoplasmic membrane or plasma membrane and from there outside of the cell, this phenomenon is called exoelectrogenesis. These photogenerated charge carrier (protons and electrons) is collected in two electrodes by using a bio-photoelectrochemical system.

Algae are the potential feedstock for producing various forms of bioenergy [2], such as bioelectricity [3], biofuel [4], biohydrogen [5], and other kinds of energy. The major advantage of algal energy harvesting is that they do not require any arable land or potable water for cultivation. Over and above that, most of the algal species are not suitable for human or animal consumption, as a result, won't create any negative impact on the food chain. Most importantly algae can be easily cultivated on a large scale in any seasonal conditions, thus the resources will be highly sustainable and reliable for future energy production. Algae also have the potential for environmental remediation by mitigating atmospheric CO_2 levels and removing contaminants from waste water [6], over all the use of algae in live cell-based energy harvesting systems is showing a new avenue for a cost-effective and sustainable approach to energy production [7]. Algae are the primary producers that can grow naturally in any aquatic habitat such as any stagnant wastewater, drains, ponds, rivers, oceans, etc. Algae can survive in a wide range of temperature and light intensities; they can tolerate a wide range of salinity and pH values. Many literatures supports the blue-green algae (cyanobacteria) and some other microalgae species are promising candidates for future bioenergy technology. These types of photovoltaic devices have the potential for application in bioelectronics devices and human electronic interfaces [8,9] The Internet of Things (IoT) is a vast network of small computational devices that are deployed in various environments and connected to different "things" for sensing and transmitting data [10]. (The IoT-based devices require minimum power which is run often by conventional batteries. These algal photo voltaic devices are desirable to power various kinds of Internet of Things (IoT) devices through energy harvesting instead of energy storage [11].

One significant issue with powering such a massive network of IoT devices is that many consume very little power and are often battery-powered. However, relying on lithium-ion batteries to power one trillion IoT devices would require more lithium than the world's annual production, which is unsustainable. Furthermore, other battery types would also require significant natural resources or routine recharging and replacement, leading to negative environmental impacts. Therefore, it is desirable to power IoT devices through energy harvesting instead of energy storage. An ideal energy harvesting system would provide enough power for continuous sensing, use inexpensive and readily available materials, and avoid toxic components. It has already been reported by P Bombelli et al. that IoT-based small computational devices are powered with algae-based photosynthetic power generators [12]. There is much literature on bio photovoltaics using microalgae and cyanobacteria [13]. In our previous studies, we have described the harvesting of photocurrent from cyanobacteria *Nostoc commune* [14] which provides a good knowledge of how photosynthetic microorganisms can act like a self-powered bio photodetector. Electricity generation

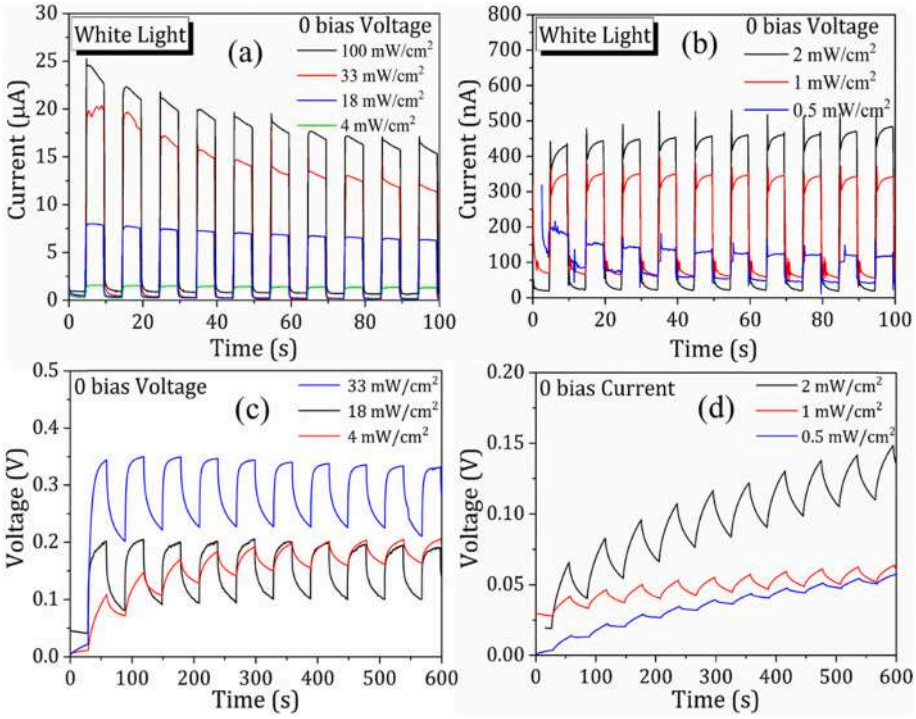

Fig. 4. a-b) time-dependent photocurrent (I-t) and c-d) Time-dependent photovoltage (V-t) for the various incident white light power intensities of the device FTO/TiO_2/Pithophora/Carbon.

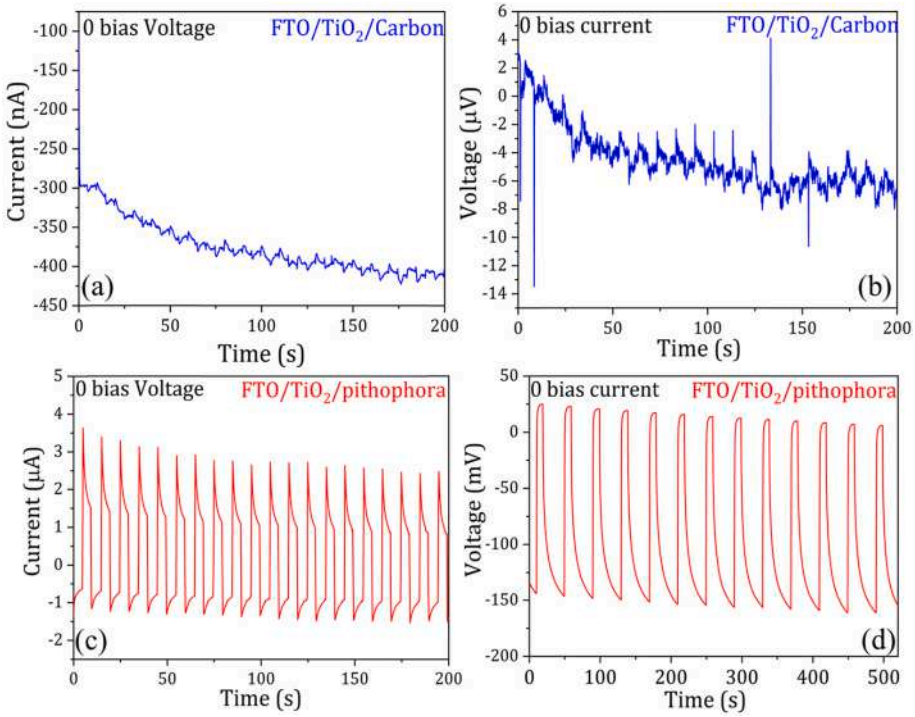

Fig. 5. a) Time-dependent photocurrent (I-t) and b) Time-dependent photovoltage (V-t) for the device FTO/TiO_2/Carbon without algae, c) Time-dependent photocurrent (I-t) and d) Time-dependent photo-voltage (V-t) for the device FTO/TiO_2/Pithophora without carbon under 100 mW/cm^2 incident white light intensity.

from macroalgae is not that much explored, but there are some bio-photoelectrochemical activities from macroalgae had been investigated recently [15], along with electricity generation by hydrovoltaic activity [16]. A globally found freshwater macroalgae Pithophora, bears a striking resemblance to a tangled mass of green wool, forming dense mats in algal blooms, often considered a water weed, challenging to manage due to its rapid growth which has become a compelling subject of research interest for power generation. To explore cost-effective power harnessing from readily available resources that is filamentous macroalgae *Pithophora roettleri*, while ensuring zero carbon emission towards a sustainable future.

Algae can be classified either based on their pigments or based on

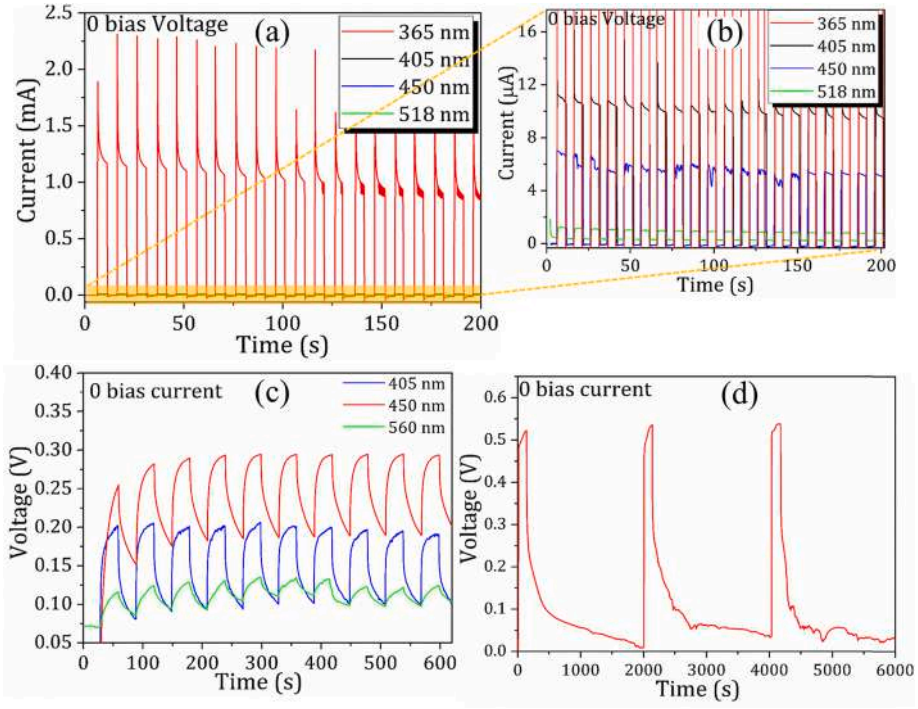

Fig. 6. a) Time-dependent photocurrent (I-t) and b) Maximized view of the I-t curve, c) Time-dependent photovoltage (V-t) for the various incident light energies having an intensity of the 10 mW/cm^2 for the device FTO/TiO_2/pithophora/Carbon.

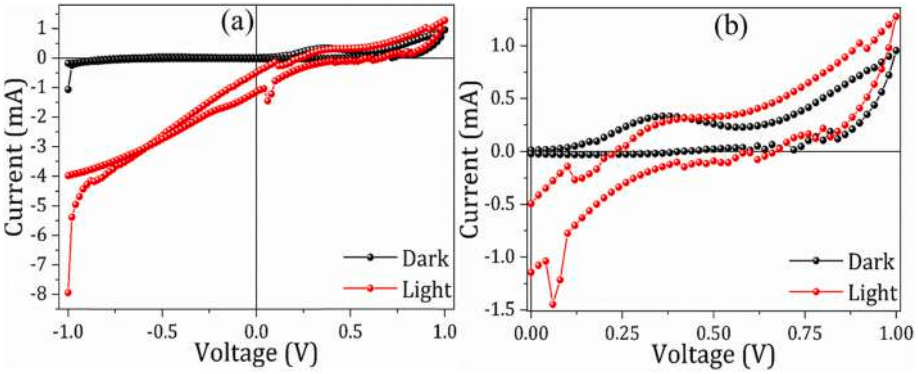

Fig. 7. a) I–V graph, b) maximized view of I–V graph of the FTO/TiO_2/Pithophora/Carbon device under dark and 365 nm light illumination conditions.

their size. Size-based classification includes macroalgae (seaweed), which are multicellular and visible to the unaided eye, and microalgae, which are single-celled and microscopic. Microalgae either be prokaryotic, similar to blue-green algae(cyanobacteria), or eukaryotic, similar to green algae (Chlorophyta), and can only be seen under a microscope, whereas macro algae can be classified into 3 major groups, are Chlorophyta or green algae, Rhodophyta or red algae and Ochrophyta or brown algae [17].

BPV technology has the potential to be a sustainable and environmental friendly alternative to conventional solar cells, as it does not require the use of expensive or toxic materials and can be grown using renewable resources. However, current BPV technology still faces challenges such as low efficiency, scalability, and stability, which need to be overcome before it can be widely adopted as a viable energy source. Nonetheless, BPV remains an exciting area of research that holds great promise for the future of renewable energy production. The primary difficulty in developing biophotovoltaic devices lies in establishing a proper connection between the electrode and the biomaterials. Typically, researchers utilize a technique wherein they cultivate a biofilm on the electrode surface by growing algae. Due to the presence of a liquid reservoir, it is bulky in structure which is facing challenges to scalability. Here we fabricated a simple semi-solid-state device by sandwiching the live macroalgae *Pithophora* in between the positive electrode and the negative electrode. Possibly this is the first reporting work with freshwater live macroalgae and generates electricity by sandwiching it in between two modified electrodes which collect the charge carriers. The TiO_2 compact layer was used as the electron transport layer [18] and carbon was used as the hole transporting layer or electron injecting layer. TiO_2 compact layer or hole blocking layer was well studied for electron transport layer for solid-state DSSC, perovskite solar cells and transparent thin film solar cell [19]. The fabricated device is then characterized by current voltage measurement in dark and in light conditions which shows excellent output. It has already been reported that whole cyanobacterial organisms are the very sturdy type, and show long lifetimes of multiple months [20]. Here the macro algae-based fabricated device has also shown good photo response for longtime.

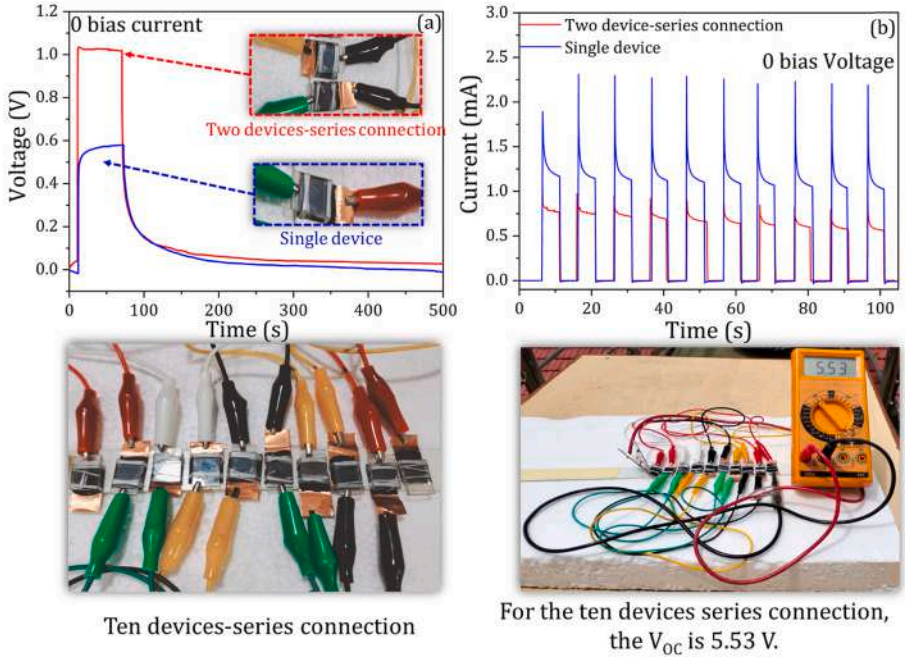

Fig. 8. a) V-t graph, b) I-t graph of the single and two FTO/TiO_2/pithophora/Carbon devices joined in a series connection, c) 10 devices series connected image, d) Series connected 10 devices measured V_{OC} under direct sunlight illumination image.

2. Experimental

2.1. Materials used

Green freshwater filamentous macroalgae Pithophora species, Titanium (IV) Isopropoxide, purchased from Sigma Aldrich, Fluorine-doped Tin Oxide (FTO) coated transparent conducting oxide (TCO) glass substrates and copper foil were purchased from Sigma Aldrich and commercial activated carbon paste were used.

2.2. Algae collection isolation

The filamentous branched green macroalgae were collected from the local pond located inside the campus of Amrita Vishwa Vidyapeetham, Coimbatore, India. It often resembling a tangled mass of cotton or wool-like growth which is very coarse to the touch and commonly known as horse hair algae. Naturally collected algae were initially cleaned by hand picking process and then washed with tap water more than 20 times. Washed and cleaned algae were centrifuged for 10 min, and separated algae were washed with deionized water 15 times. The clean and isolated algae were investigated using a CHi 20 Olympus microscope. The algae were characterized by different techniques as described in SI1.

2.3. Device fabrication

We fabricated the device by sandwiching the freshly collected macro algae *Pithophora roettleri* in between TiO_2-coated FTO glass and activated carbon-coated copper foil. Before the device fabrication, the electrode's FTO-coated glass was cleaned with a diluted soap solution. Subsequently, it was ultrasonically cleaned in acetone, ethanol, and deionized water separately for 15 min and then dried on the other hand copper foil was cleaned with diluted hydrochloric acid. Then we deposited a TiO_2 blocking layer on top of the commercially available FTO-coated glass and deposited coconut shell activated carbon as a positive terminal on the cleaned copper foil. The collected fresh water-green macroalgal species were crushed and made into very small fragments. After that, these algae were sandwiched in between the electrodes, of TiO_2-coated FTO (bottom) and activated carbon-coated Cu (top) electrodes. Details of the electrode fabrications are given in the SI2.

2.4. Characterization details

The UV–Vis absorption spectra of *Pithophora* were measured using a Shimadzu (UV-1800) spectrophotometer in 1 cm path-length square cuvettes. A few fragmented pieces of *Pithophora* were dispersed in DDW for the UV–Vis investigation. The electrical measurements of the device were done using the Keithley-2450 source meter.

3. Results and discussion

3.1. Microscopic investigation–Genome sequencing and phylogenetic analysis

The naturally grown collected algal filaments were green to greenish brown (Fig. 1a), filaments are irregularly branched and contain terminal and intercalary akinetes (Fig. 1b), the algal cells were slender and cylindrical containing very thin cell walls without layers. Single reticulated chloroplast with numerous pyrenoids was present in each cell (Fig. 1b). Apical cells are mostly conical and rounded. These observations were supported with previously reported data [21]. From this microscopic observation it concludes that the alga belongs to the family of Pithophoraceae and the genus is *Pithophora.* For the species identification, we studied partial 18s rRNA sequence and analyzed the phylogenetic relationship, algae samples were subjected to DNA isolation using the EXpure DNA isolation kit, a product developed by Bogar Bio Bee stores Pvt Ltd. The isolated DNA was then amplified using Polymerase Chain Reaction (PCR) with specific enzymes to target desired cloned or genomic DNA sequences. Subsequently, the amplified PCR product was subjected to sequencing using the ABI PRISM® BigDyeTM Terminator Cycle Sequencing Kits, which utilize AmpliTaq® DNA polymerase (FS enzyme) from Applied Biosystems., which confirmed that the species is *Pithophora roettleri* [16,22]. The UV–Vis absorbance spectra of the *Pithophora roettleri* is recorded using a UV–vis absorption spectrometer from the range of 200–800 nm and the resultant spectrum

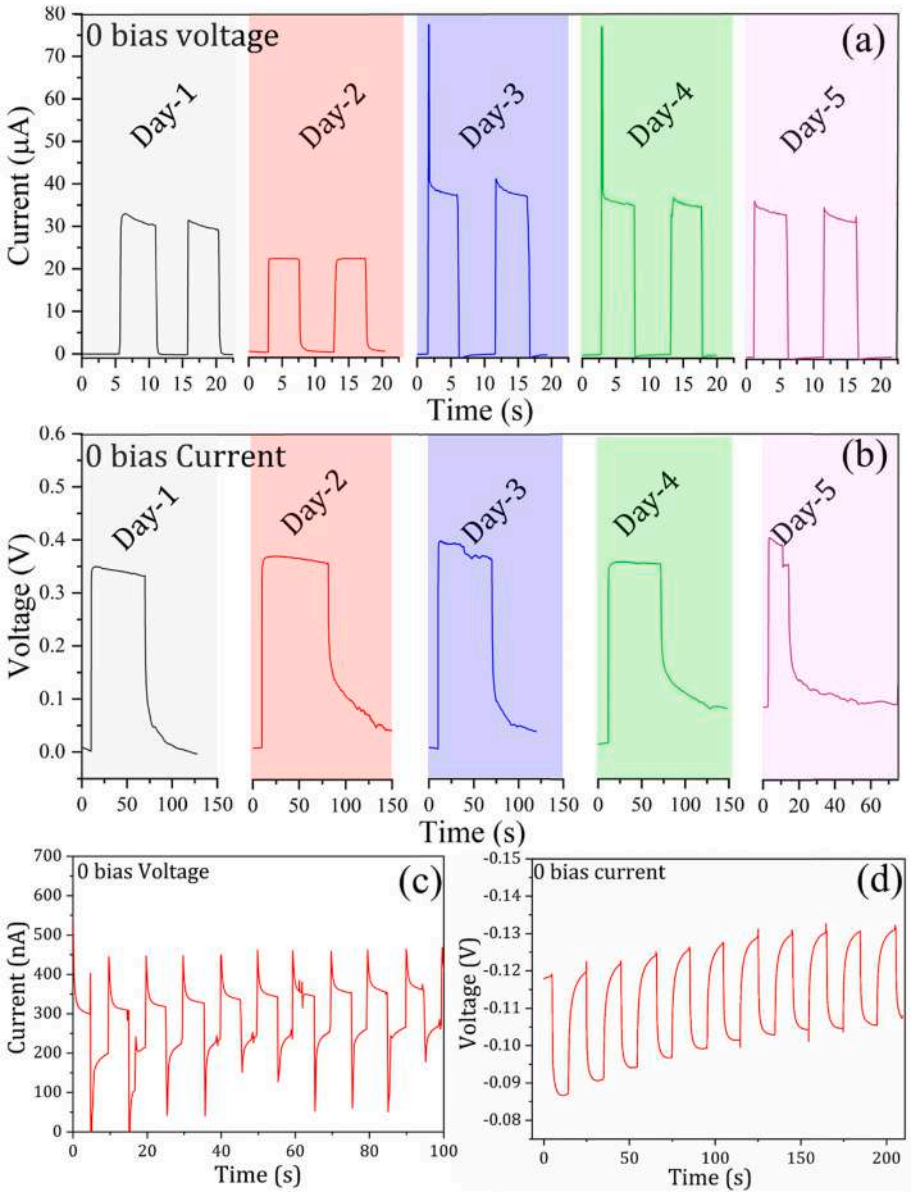

Fig. 9. a) I-t graph, b) V-t graph for the 5 days, c) I-t graph, d) V-t graph of the FTO/TiO_2/pithophora/Carbon devices after 5 months under white light illumination.

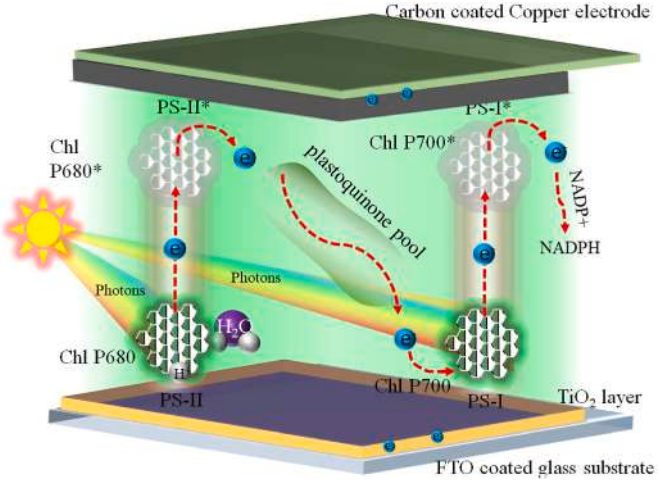

Fig. 10. Schematic presentation of the photosynthetic charge carrier generation and collection by exo-electrogenesis process.

is shown in Fig. 1c. The maximum light absorption of the algae is in the UV region which extended till visible region around 550 nm. Further around 680 nm, again one more absorption peak was noticed. The observed spectrum is following the previous reports [23,24]. Several peaks in the absorption curve occur because of the assortment of pigments found in green algae. It is well known that green algae contain chlorophyll *a* and *b* as main photosynthetic pigments along with some additional accessory pigments like carotenoids and xanthophylls. As a result, when measuring the absorption of light by green algae across different wavelengths, these pigments collectively contribute to the distinct peaks in the absorption spectrum. This wider range of absorption of light energy across a broader spectrum concludes that the algae can absorb UV–Vis light and can create photo charge carriers for solar cell application. The fabricated solar cell device schematic diagram is shown in Fig. 1d. Different layers of the device are explained in supporting information (SI3).

The different layers of the fabricated device are also characterized to understand the device's performance. The XRD pattern of TiO_2 and activated carbon thin film is shown in Fig. (SI4a-b). The prepared TiO_2 thin film shows anatase phase, having the unit cell of tetragonal

structure with I 41/amd space group. The crosssectional FESEM image revealed the thickness of the film is ~200 nm (SI5). Further, the XRD pattern of actived carbon assured the formation of crystalline structures of the graphitic carbon. The activated carbon's crystalline structure was confirmed by observing a sharp peak around 26°, indicating the superior alignment of disordered graphitic carbon layers in a turbostratic structure.

3.2. Current-voltage measurement of the device

The current vs voltage (I–V) curve of the algal PV device was recorded in the voltage scan cycle range of −1 V to +1 V under dark and upon illumination with the white light of intensity 100 mW/cm^2. The measured I–V loop is shown in Fig. 2a. The device exhibits a typical non-ohmic behavior ascribed to the build-in asymmetry potential across FTO/TiO_2/*Pithophora*/Carbon device. Further, for the voltage sweep of −1 to +1 V and +1 to −1 V, the current curves attain different path-forming hysteresis curve behavior. It is quite obvious that the activated carbon is used as electron injection layers in algal PV devices and due to higher surface area its stores more charge carriers in their active sites. At dark conditions also the device exhibits some I_{SC} of ~35 μA and V_{OC} of ~0.5 V because of the hysteresis. However, under white light illumination, the I_{SC} reaches the value of ~81 μA and V_{OC} of ~0.58 V. The V_{OC} was enhanced due to photosynthesis charge carrier generation as shown in Fig. 2b. The photoactive algae contribute a major role in the creation of extra charge carriers through the photosynthesis process. In the presence of light, water hydrolyzes and generates electrons and H^+ ions. These generated charge carriers reached to the electrode probably by exoelectrogenesis process, the detailed mechanism is described in the later section. Hence, under light illumination enhanced current was observed. However, due to the hysteresis behavior of the I–V curve, it was unclear to identify the exact I_{SC} and V_{OC} produced by the algal PV device. Therefore, the I_{SC} and V_{OC} were precisely observed by measuring I-t (current vs time) and V-t (voltage vs time) curves under dark and light conditions.

To explicate the cycle stability and the short circuit current (I_{SC}) of the PV device, at zero bias voltage, the time-dependent current (I-t curve) was recorded under the white light intensity of 100 mW/cm^2 shown in Fig. 2c. While the I-t measurement, the incident white light is chopped between the ON and OFF state with a regular interval of 5 s. Once the light was irradiated, the current increased abruptly and then reached the maximum within a time interval of less than 1 s, and it fell quickly upon turning off the light. The ON-OFF cycle was repeated 116 times, the observed photocurrent was initially at ~23 μA without applying any voltage. Then, it gradually decreases with time and reaches the saturated current value of ~9 μA and then gets stabled at that current. The reason behind this might be due to the dehydration of water present in the algal species which suppresses the carrier's generation and transportation. It was confirmed by adding a few drops of water during the measurement, after the rehydration, the photocurrent again started increasing in a device shown in Fig. 2d. Which established that a constant supply of water will help to perform the device with better efficiency.

The open circuit photovoltage (V_{OC}) of algal PV devices was studied from the time-dependent voltage (V-t) curve (Fig. 3a) recorded at zero bias current by chopping the light ON for 30 s and the OFF for 600 s periodically and repeated 15 cycles. In this measurement, the device voltage was allowed to get saturated under the illumination of white light. Unfortunately, the observed V_{OC} in the I–V curve due to some charge storage is not reflected in this V-t measurement. The attained maximum photovoltage in this V-t measurement is ~0.35 V within the 30 s shown in Fig. 2b. Subsequently when the light was turned OFF, the photovoltage is reaching the dark state rapidly, it takes around 600 s to reach the dark state voltage of 0.025 V; due to charge stored in active sites of carbon layer which releases very slowly, that implies the present device structure can work simultaneously for energy conversion and storage. However, the observed photovoltage is higher than reported bio-photovoltaics as described in Table 1.

Further, the algal PV device performance was studied for various intensities of white light shown in Fig. 4a and b. Even for the various intensities 0.5, 1, 2, 4, 18, 33, and 100 mW/cm^2 also the device exhibits a better photocurrent as 0.139, 0.34, 0.45, 1.38, 7.95, 20.01, and 23 μA respectively. This implies that the PV device is highly sensitive to the low white light intensity of 0.5 mW/cm^2 and exhibits a good photocurrent of 23 μA for 100 mW/cm^2 light signal. There is no reduction in the magnitude of the photo-generated current density with time for lower incident light intensity. Hence, the reduction in amplitude of the current at higher light intensity was probably due to the high temperature making the device dehydrate. Moreover, for the same various white light intensities, the photovoltage was also recorded at zero bias applied current. Now the light was toggled between ON and OFF states with a duration of 30 s periodically. But here the dark voltage is not coming to the ground state as the charges are stored in carbon and it takes a longer time (~600 s) to come to its initial state. Hence the observed photovoltage is not saturated and triangle in shape as shown in Fig. 4c and d.

Further, to confirm the photo-response of the device without algae, the device performance was studied and shown in Fig. 5a and b. From the time-dependent photocurrent (I-t) and photo-voltage (V-t), we could see no significant photocurrent or voltage observed during the light ON-OFF time. This signifies that algae only contribute a major role in producing a photogenerated charge carrier through the photosynthesis process; without *Pithophora*, there is no photocurrent and voltage. Further, without carbon also, the device performance (I-t and V-t) was analyzed and shown in Fig. 5c and d. The attained maximum photocurrent (ΔI) and photo-voltage (ΔV) of the TiO_2/*Pithophora*/Cu device are ~2.56 μA and 0.171 V, respectively. It is important to notice here that, in the V-t graph the dark state is the same as it started is due to without carbon no charges had been stored.

To find the photoresponse performance of the TiO_2/*Pithophora*/carbon device under the different wavelengths 365, 405, 450, and 518 nm of the incident light, the I-t and V-t measurement has been done and is shown in Fig. 6. The observed photocurrent and photovoltage values of the device under 365, 405, 450, and 518 nm are 1.19 mA, 10.19 μA, 5.6 μA, 0.97 μA, and 525 mV,115 mV, 105 mV, 37 mV respectively. It is noteworthy to mention that performance of the device is much better in 365 nm light illumination compared to white light illumination.

Since the device exhibits better performance (I-t, V-t graph) under 365 nm illumination light, further I–V curve is also recorded and shown in Fig. 7a. The voltage sweep from −1 to +1 V, current vs voltage curve predicts that the device possesses an outstanding performance when the reverse voltage increases. This is similar to the photodiode curve nature; an increase in applied reverse voltage causes to increase in the size of the depletion region. This creates a high electric field across the junction, effectively increasing the separation of photo-generated charge carriers. From the maximized I–V graph, Fig. 7b, the attained I_{SC} and V_{OC} of the device is ~1.2 mA and ~0.6 V, which also reflects in the I-t and V-t curves of the device. A statistical set of data for 18 different device were given in the SI3, there is slight variation in the performance from device to device because of the variation of packing in the algal biofilm.

3.3. Series-connection of PV device

This fabricated photovoltaic cell can be practically applied by connecting the individual device into series and parallel combinations. As an initial stage, just two devices were connected into series, as shown in Fig. 8a inset image. From the recorded V-t curve, it is found that the V_{OC} of the single device is ~0.5 V. Once it is connected in series, the voltage was doubled as ~1 V. Likewise, the device's I_{SC} was also recorded, shown in Fig. 8b. The current value of a single device is ~1.3 mA, whereas, for the series connection, it decreased as 0.8 mA due to diffusion of photocurrent in two devices to get equalize. Moreover, the

ten devices were connected in series combination as displayed in Fig. 9c, and it was tested under direct sunlight. We could see that the individual voltage of the device was added up and shows cumulatively 5.53 V. This signifies that our designed device is more reliable and practically useable in daily life.

3.4. Device stability

This technology can be applied to the fabrication of nontoxic solar cells. It leverages the natural photosynthetic process to provide an inexpensive and higher energy yield replacement for silicon-based solar cells. Furthermore, under natural sunlight, 10 fabricated devices in a series connection are capable of producing 5.53 V, which is desirable to power IoT-based devices through energy harvesting from solar energy. Biophotovoltaics devices need two chambers with a proton-conducting membrane but the present device structure is a more simple one similar to a sandwich device with a very thin layer of aqueous algal film. Though there are some reports on the solar cell or biohybrid solar cell with inorganic and biomaterials hybrid as photo absorber materials, most of them extract the photosystem and incorporate it inside the device, which raises the question of stability and practical applicability.

To study that, the device photoresponse was studied periodically for 5 days. Each day, before measuring the device's performance the water drops were injected into the algae part. The resultant I-t and V-t data for the 5 days are shown in Fig. 9a and b. From the figure it is clear that there is no reduction of photocurrent (ΔI) and photovoltage (ΔV) even after 5 days, I and V remain the same. Moreover, the present device exhibits a long lifetime, we kept the device after performance analysis under the natural laboratory environment (under the drawer inside two Petridis), and we observed similar performance from the device after 6 months shown in Fig. 9c and d. As the device was dry, we added one drop of water in between the two electrodes so the inside algae exhibited bioactivity. We observed a bit of low current, probably some of the algal cells died because of lack of water.

3.5. Working mechanism

The above discussions on the device performance established that the macroalgae Pithophora roettleri is a promising candidate for solar energy harvesting via a bio-photovoltaics system. The quasi-sandwich device with an aqueous biofilm of Pithophora roettleri in between two electrodes was able to electrolyze the water in the presence of sunlight and the photogenerated electron reached the electrode by exo-electrogenesis activity to develop electrical power. During the photosynthesis process, chlorophyll molecules absorb photons, become excited, and move to higher energy levels. The excited chlorophyll migrates to the reaction center of PS II The energized electron is relaxed from the reaction center and accepted by the first electron carrier in the photosynthetic electron transport chain (Fig. 10). The first electron carrier becomes reduced and the reaction center becomes oxidized. Due to the loss of electron, an electron hole is created in the PS II reaction center. The high-energy electron passes to NADP + through the plastoquinone pull and eventually reduces NADP + to form NADPH.

The electron hole of PS I is replaced by an electron from PS II and the PS II electron hole is filled by the electron derived by photolysis of water. So it is very clear that the entire photosynthetic electron transport starts from a water molecule and ends with the reduction of NADP + to create NADPH and ATP. Probably a fraction of the NADPH and produced electrons were coming out from the PETC by exoelectrogenic activity and may be transported to the edge of the cell wall to the electrodes which are characterized by current-voltage measurement of the device in dark and in light conditions. We used here TiO2−coated FTO glass as an electrode, where the TiO_2 compact layer functions as a hole blocking and electron transport layer. On the other side, used carbon-coated copper, as a layer that transports holes. During the exoelectrogenesis process, the released electrons are injected into the Fermi energy of TiO_2 and eventually reach the FTO (current collector). Simultaneously, to sustain the Photosynthetic Electron Transport Chain (PTEC), one electron is introduced into the system via the carbon-coated copper the same process will be repeated.

The schematic diagram below exhibits the working mechanism of the device. In the presence of light, the photo-generated charge carriers are responsible for the generation of photocurrent and photovoltage.

Also, we compared the performance of our device with some reported devices with a modified electrode of bio-photovoltaic device, and the analyzed results were tabulated below.

4. Conclusion

The present work demonstrates the generation of bioelectricity from freshwater filamentous macro-algae, *Pithophora*. The device used in this study consisted of a sandwiched structure, with ruptured macroalgae in between a carbon-coated copper electrode and a TiO_2-coated FTO electrode. The device was found to generate an open-circuit voltage of 0.35 V and a short-circuit current of 10.19 μA. The performance of the device was further enhanced when exposed to UV light with a wavelength of 365 nm. Under these conditions, the device exhibited a photocurrent of 1.25 mA and a photovoltage of 0.5V without any applied bias. The device also performed well under ambient conditions, such as natural sunlight, indicating its potential as a power generator. A series connection of 10 devices was shown to enhance the voltage output to 5.53V. These findings suggest that bioelectricity generated from the photosynthesis process of macroalgae has the potential for use in low-power IoT-based devices. Overall, this study provides important insights into the potential use of macro-algae as a source of renewable energy and highlights the importance of exploring alternative energy sources to reduce our reliance on fossil fuels.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jsamd.2024.100674.

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