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Photoelectric evaluation of dye-sensitized solar cells based on prodigiosin pigment derived from *Serratia marcescens* 11E

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ABSTRACT

Prodigiosin, a natural pigment produced as a secondary metabolite by the non-photosynthetic bacterium *Serratia marcescens*, was tested as a sensitizer in dye-sensitized solar cells (DSSC). The strain *S. marcescens* 11E, which was isolated from a natural spring located in the northeastern Mexican state of Nuevo Leon, was cultivated on peanut oil broth 1% v/v, a culture medium which is known to enhance the production of prodigiosin. The resulting pigment was extracted with chloroform and identified as prodigiosin based on the spectroscopic and structural characteristics obtained by UV–Vis spectrophotometry along with FTIR and 1H NMR spectroscopies. The initial absorbance decomposition test performed on the bacterial pigment demonstrated that prodigiosin exhibited high photostability after five days, while the photovoltaic performance test of the sensitized DSSC, resulted in an open voltage circuit of 560 mV, a current density of 0.096 mA/cm^2, and efficiency of 0.032%. Structurally, the DSSC consisted of a titanium dioxide (TiO_2) photoanode sensitized with the pigment by direct adsorption, an electrolyte containing a redox pair I^-/I^{3-} and a cathode or counter electrode prepared from a carbon paste. Since the overproduction of prodigiosin can be easily achieved on a large scale through the rapid fermentation of agro-industrial residues throughout the year without the need to allocate surfaces for the cultivation of pigment-producing plants or wait for specific seasons for their cultivation, our results suggest that prodigiosin could be considered an excellent candidate to be used in the development of a low-tech, low-cost DSSC.

1. Introduction

Throughout evolution, bacteria have adapted to all the ecosystems present on the planet [1]. To do so, they had to develop a wide range of secondary metabolites that allowed them to colonise different ecological niches to ensure their survival [2]. Among the heterogeneous group of secondary metabolic products that exist among prokaryotes, pigments confer important adaptive roles, by functioning primarily as photoprotective agents for the cell [3]. However, it is known that some of them participate in the cellular respiration process, particularly within the electron transport chain [4], or even act as intermediary mediating agents in redox reactions when cells interact with their surrounding environment [5]. These distinctive physical and chemical properties of bacterial pigments can be extrapolated from biological systems to emerging technologies designed to generate electricity. In this sense, bacterial pigments have managed to be protagonists in the development of microbial fuel cells [6] and more recently, in dye-sensitized solar cells (DSSC) [7]. As the development of DSSC progresses, bacterial pigments have been shown to have several significant advantages over plant-derived pigments, such as the capability to be produced on a large scale through rapid fermentations that can be carried out throughout the year, along with their excellent stability and solubility [8]. Besides,

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there is an increasing concern that large-scale production of plants intended for the extraction of their pigments could cause severe problems to the ecosystem, including deforestation and infringement to the diversity of local species [9]. Therefore, in recent years, it has been proposed that bacterial pigments could be an excellent alternative for the manufacture of DSSC [10].

Among the great diversity of bacterial pigments known to date, prodigiosin, distinctive of bacteria such as *Serratia marcescens* [11] and *Streptomyces coelicolor* [12], stands out for being known since ancient times and studied extensively since the beginning of the nineteen century [13]. This pigment which is commonly localized in extracellular and cell-associated vesicles as well as intracellular granules [14], possesses a chemical structure characterized by the presence of three pyrrolic rings responsible for the generation of an intense red colouration, very similar to blood (Fig. 1).

Due to its structural similarity with porphyrins [15], the applications given to this pigment have been mainly directed towards biomedicine, standing out as a potent antibacterial [16], antiviral [17] and anticancer agent [18]. However, having a chemical structure rich in *pi* electrons and a series of electron donor pyrrolic nitrogens, this pigment is capable of interacting with metal ions to form coordination compounds [19] or transfer electrons from its photo-excited state to the conduction band of metal oxides to generate a current, as occurs in many natural pigments [10,20]. This, together with recent research that has resulted in the optimization and overproduction of prodigiosin using agro-industrial residues [21,22], make this molecule an ideal candidate to be investigated as a sensitizer for DSSC, which could result in the reduction of their production costs and facilitate their future commercialization. In this sense, this work seeks, in addition to encouraging the development of this promising technology through the generation of an alternative for the construction of low-cost and low-tech DSSC, to expand the existing range of materials of microbial origin that can be used as photosensitizers, expanding the small spectrum of bacterial pigments that have been investigated to date, which only includes the xanthophyll pigments extracted from *Chryseobacterium* sp [23]. and *Hymenobacter* sp. [10], eumelanin from *Streptomyces fildesensis* [24] and bacterioruberin from *Halobacter salinarum* [25].

2. Materials and methods

2.1. Bacterial strain and prodigiosin production

S. marcescens 11E, a wild-type bacterial strain previously isolated from the Bustamante National Park located on the northeastern Mexican state of Nuevo León [22], was reconstituted from a frozen stock by incubating it at 28 °C for 24 h on LB broth (100 mL). This culture was used to inoculate at 2% v/v a sterile peanut oil broth (100 mL), consisting of peanut seed oil (1.0 g) disperse in distilled water (100 mL) and sterilized by autoclaving at 121 °C and 15 psi for 15 min [26]. After inoculation, the prodigiosin production was stimulated by incubating the cells at 28 °C and 150 rpm for 36 h in a MaxQ 4000 orbital shaker (Thermo Fisher Scientific; Waltham, USA). Microbial growth was followed by measuring absorbance at 620 nm using a Cary 50 spectrophotometer (Agilent Technologies; Santa Clara, USA), while prodigiosin production was monitored by measuring the pigment's maximum absorbance peak at 539 nm. At the end of the experimentation time, the bacterial cells were harvested by centrifugation at 4000 rpm and 8 °C for 10 min using a Beckman Avanti 30 high-speed centrifuge (Beckman Coulter, Inc.; CA, USA). Ultimately, prodigiosin was extracted from the centrifuged cell pellets with chloroform, assisted with sonication treatments of 10 30-s periods with 2-min intervals at 16 kHz using a Fisherbrand™ Model 120 Sonic Dismembrator (Thermo Fisher Scientific; Waltham, USA). A final centrifugation step was used to removed cell debris, and the prodigiosin-rich chloroform crude extract was evaporated using an RV 3 Rotary Evaporator (IKA Works GmbH & Co. KG.; Staufen im Breisgau, Germany) for storage until required.

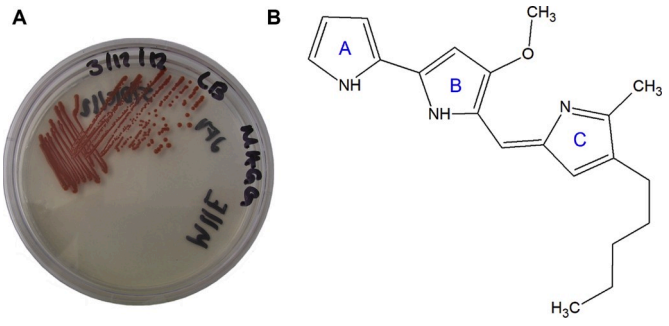

Fig. 1. (a) *Serratia marcescens* 11E grown on LB agar; (b) Chemical structure of prodigiosin, denoting the pyrrolic rings A, B, and C.

2.2. Prodigiosin purification and characterization

The prodigiosin-rich dried crude extract was dissolved in chloroform (1 mL) and purified by column chromatography using silica-gel equilibrated with chloroform as the solid matrix. A solvent system comprising a mixture of chloroform:methanol (9:1, v/v) was used as the mobile phase. The purity of the resulting pigmented eluent was evaluated using a Waters 2695 Alliance HPLC (Waters Corporation; Milford, USA) on a C18 column (5 μm ODS, 250 mm × 4.6 mm), with a mixture of chloroform:methanol (9:1, v/v) as mobile phase. The characterization of the purified bacterial pigment consisted of a full scan of the UV–Vis spectrum using the Cary 50 spectrophotometer in the wavelength range between 300 and 800 nm, followed by an infrared analysis using a Spectrum 100 FTIR spectrometer (PerkinElmer Inc; Waltham, USA) in the region between 4000 and 650 cm^{-1} with a resolution of 50 scans at 4 cm^{-1}, using a KBr window for solutions. Finally, the bacterial pigment characterization was followed by a 1H NMR analysis using a Mercury-200 NMR spectrometer (Varian Inc., Palo Alto, USA) working at 200 MHz. Prodigiosin production yield was determined as the dry weight of the intracellular prodigiosin extracted per litre of culture.

2.3. Prodigiosin photostability evaluation

The photostability of the purified prodigiosin was determined by exposing the pigment to continuous light (~70 mW cm^{-2}) for 120 h, monitoring the pigment decomposition in absorbance every 12 h at 539 nm using the Cary 50 spectrophotometer. These experiments were performed at 18 °C to avoid possible evaporation of the solvent. The pigment concentration was calculated as mg mL^{-1} from a calibration curve carried out using prodigiosin hydrochloride acquired from Sigma-Aldrich.

2.4. Construction of the sensitized photoanode and cyclic voltammetry evaluation

All the electrodes used in the fabrication of the DSSC of this study were based on Fluorine doped Tin Oxide (FTO) conductive glasses (TEC15; 3 × 3 × 2.2 mm; MTI Corporation; Richmond, USA), which were cleaned with distilled water followed by an ultrasonic bath in a solution of acetone-isopropanol (1:1, v/v) for 30 min before use.

The construction of the photoanode was prepared according to the method described by Al-Alwani et al. [27], in which commercial TiO_2 nanopowder (TiO_2, anatase, 99.5%, Sigma-Aldrich, Mexico, 3.0 g) were mixed with nitric acid (0.1 M, 6 mL) and poly (ethylene glycol) (3 mL) in a mortar and pestle until a white suspension was formed. To this solution, some drops of Triton X-100 were added, stirring until the suspension formed a suitable paste. The TiO_2 paste was blended over a 1 cm^2 of the active area of the FTO conductor glass and then sintered at 450 °C for 30 min in a muffle furnace. Once dried, the TiO_2 coated electrode was

immersed in a prodigiosin solution (1.0 mg mL^{-1}), to which the amount of prodigiosin absorbed in TiO_2 film was quantified spectrophotometrically by measuring the decay in the pigment's absorbance every 45 min at 539 nm and expressed in terms of concentration as mg mL^{-1} according to the linear regression equation obtained from the calibration curve. After 4 h of immersion, the non-adsorbed dye was washed up from the photoanode with anhydrous ethanol.

After the completion of the photoanode, the prodigiosin redox profile was evaluated by cyclic voltammetry, which was carried out on a CHI700E electrochemical workstation (CH Instruments Inc.; Bee Cave, USA), using an ethanol/$NaClO_4$ 0.1 M (50:50) solution as a supporting electrolyte and a scan rate of 0.1 V/s. The cyclic voltammetries were carried out in a three-electrode scheme consisting of our sensitized electrode as a working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. To calibrate the results of the E_{ox} or E_{red}, ferrocene was used as an external standard. The evaluation was based on the empirical relation $E_{LUMO} = [(E_{red}- E_{1/2(ferrocene)}) +4.8]$ eV and $E_{HOMO} = [(E_{ox}- E_{1/2(ferrocene)}) +4.8]$ eV [28].

2.5. Dye-sensitized solar cell assembly

Following the construction of the photoanode, a counter electrode was fabricated to analyse the effect that the cathode material has on the efficiency of the DSSC. This cathode was obtained by spreading a commercial carbon sensor paste (Gwent Group Ltd; Pontypool, UK) onto the conducting surface of the FTO conductor glass (MTI Corporation; Richmond, USA). Finally, the DSSC was assembled placing by capillarity the electrolyte solution, prepared by dissolving KI (0.5 M) and I_2 (0.05 M) in ethylene glycol to form the iodide/triiodide pair (I^-/I^{3-}), between the photoanode (FTO/TiO_2/prodigiosin electrode) and the cathode (carbon counter electrode).

2.6. Evaluation of the performance of DSSC sensitized with prodigiosin

Once assembled, measurements to register I–V curves and time-dependent photocurrent responses were performed in triplicate using a Model 700E Series Bipotentiostat (CH Instruments Inc.; Bee Cave, USA) coupled to a Suntest XLS+ solar simulator (Atlas Material Testing Technology; Mount Prospect, USA) under standard test conditions of temperature and irradiance at a single sunlight intensity (irradiation of ~100 mW cm^{-2}) and 1.5 a.m. spectrum. Then, electrochemical impedance spectroscopy (EIS) measurements were performed in the dark with a frequency range from 1 Hz to 100 kHz and alternate current amplitude set at 10 mV, recorded the Model 700E Series Bipotentiostat.

From the I–V curve, corresponding to the plotting of current at a rising voltage (V), photoelectrochemical parameters such as photocurrent densities (J_{max}) and photovoltage (V_{max}) for maximum power output (P_{max}) were obtained.

On the other hand, the fill factor (FF) of the DSSC, which is a measure of series resistance and junction quality of the cell, was calculated according to the following equation [29]:

$$FF = \frac{P_{max}}{J_{sc}\ x\ V_{oc}}$$

Where P_{max} is the maximum output power, J_{sc} and V_{oc} are the short circuit currents (measured in mA cm^{-2}) and the open-circuit voltage, respectively, both obtained from I–V curve.

Finally, the conversion efficiency of solar energy to electricity (η) of the DSSC was calculated by the following equation [29]:

$$\eta = \frac{P_{max}}{P_{in}}$$

Where and P_{in} is the input power (incident light) measured in mW·cm^{-2}.

3. Results and discussions

3.1. Bacterial strain and prodigiosin production

A frozen stock of *S. marcescens* 11E was reconstituted on LB broth for 24 h, allowing the cells to reactivate for the preparation of the inoculum to be used on the prodigiosin production experiments. Under the microscope, the cells present on the culture were visualized as Gram-negative rod-shaped bacteria. This, together with the presence of the distinctive red pigmentation of the culture triggered by the tri-pyrrolic pigment prodigiosin, coincides with the phenotypic characteristics of the species [30], confirming, in turn, the biochemical and molecular characteristics previously described for *S. marcescens* 11E [22]. After 36 h of fermentation, the prodigiosin production achieved a final yield of 2 g of dried crude extract rich in red pigment.

3.2. Prodigiosin purification and characterization

The dried crude extract was dissolved in chloroform and submitted to column chromatography for its purification. The purity of the resulting pigmented eluent was evaluated by HPLC, which chromatographic profile exhibited the presence of a single peak at a retention time of 2.71 min (Fig. 2). The resulting red eluent was subjected to a full scan of the UV–Vis spectrum to determine if the absorbance fingerprint of the purified pigment coincided with that reported previously for prodigiosin. As shown in Fig. 3a, the pigment exhibited an intense, sharp peak with a maximum absorbance at 539 nm accompanied with a slight shoulder on the low wavelength limb of the curve at about 510 nm, coinciding with the historical description made by Hubbard and Rimington in 1950 [31]. As it can be observed in Fig. 3b, the FTIR characterization denoted the presence of peaks associated with prodigiosin characteristic groups, such as the sharp peak observed at 3294 cm^{-1} commonly attributed to the N–H stretches present in the heterocyclic amines of rings A and B, complemented with that observed at 1377 cm^{-1} corresponding to ϕ-N stretch adjacent to a double bond, as observed in ring C [32]. Additional significant signals were observed between 2900 and 2800 cm^{-1} which are associated with the asymmetrical and symmetrical stretching of methyl and methylene groups found in the aliphatic chain of the molecule [33], as well as those present at 2031, 1652, 1552, 1462 cm^{-1}, which denotes the presence of conjugated C=C stretches [34]. Interestingly, a signal peak denoting the presence of a C=O stretch can be observed at 1736 cm^{-1}, suggesting the presence of a carbonyl carbon instead of the expected methoxy group.

For 1H NMR (Fig. 3c), the expected signals for prodigiosin can also be observed, since a chemical shift of 0.90 and 1.65 ppm denoting a multiplet corresponding to the hydrogens of the methyl and methylene groups of the aliphatic chain present in the ring C of the molecule, alongside with the overlapping signals between 2.30 and 2.40 ppm for a singlet attributable to the CH_3 and a triplet corresponding to connecting methylene of the aliphatic chain. On the other hand, characteristic signals for the pyrrolic protons of rings A and C appear in the region between 3.70 and 4.30 ppm, while the singlet signal at 7.3 ppm can be assigned to the vinyl proton located between the ring B and C. Similar results have been reported for a new prodigiosin isolated from *Streptomyces violaceusniger* [35].

From our spectroscopic and spectrophotometric results, we can conclude that the identity of our bacterial pigment is prodigiosin. It should be noted that the complete characterization of the bacterial red pigment is still in process, and will be complemented with 13C NMR, High-Resolution Mass Analysis and elemental analysis.

3.3. Prodigiosin photostability evaluation

The photostability of the purified pigment was evaluated to determine the potential use of prodigiosin as a sensitizer for DSSC. To do so, the pigment was exposed to light (~70 mW cm^{-2}) during 96 h,

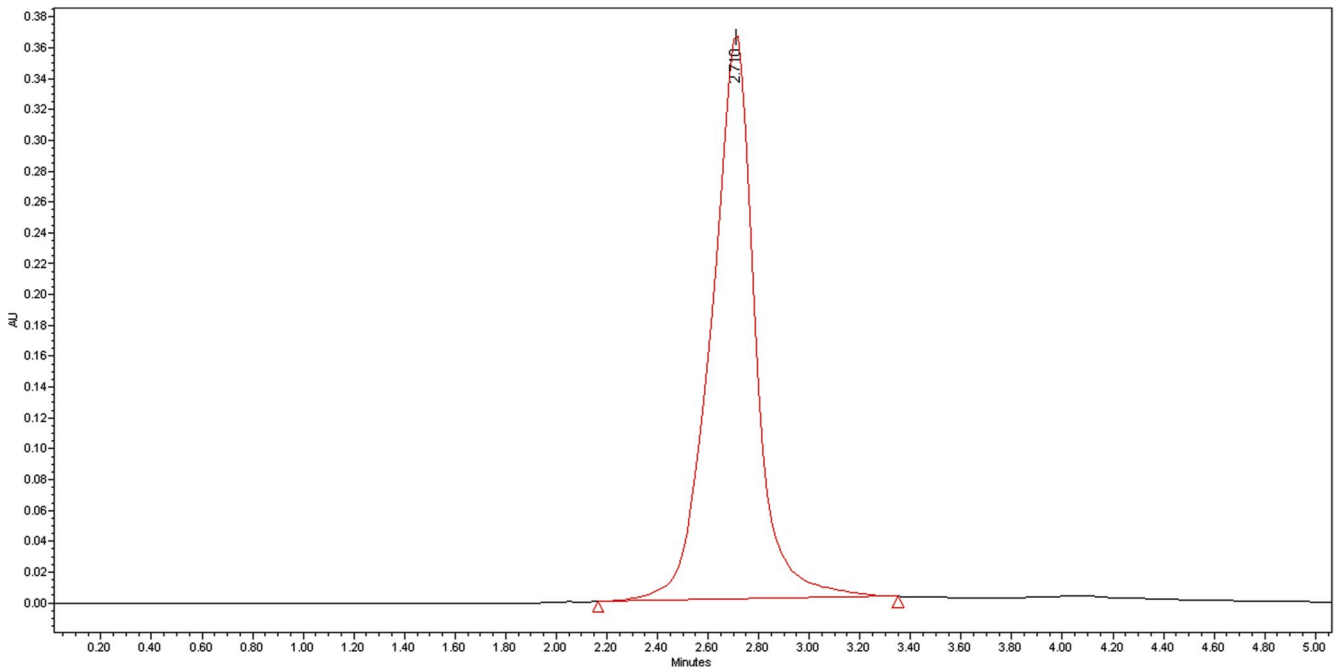

Fig. 2. The purity of the resulting pigmented eluent evaluated by HPLC at 539 nm.

measuring the decay in concentration every 12 h at 539 nm. As observed in Fig. 4, the prodigiosin produced by *S. marcescens* 11E presented high photostability, exhibiting limited degradation over the extension of the evaluation time. This result correlated with previous findings that reported the resistance of prodigiosin to light degradation [36] given that its chemical structure confers the capacity to store visible light energy [37], mainly due to the presence of the pyrrolic structures [38]. As lone pairs electrons can be conjugated with surrounding pi bonds, the pyrroles act as an aromatic structure with a hybrid resonance, provoking an extra stabilisation [39]. Therefore, as the native *S. marcescens* strain was isolated from a natural spring exposed to high-UV niche, the role of prodigiosin as a photoprotective agent for the cell can be acknowledged. Since pigments are commonly considered photostable when their concentration is maintained in 80% during the exposure test due to the integrity of its molecular structure [40], prodigiosin can be considered an excellent candidate to be used as a sensitizer for DSSC.

3.4. Cyclic voltammetry evaluation

The electrochemical behaviour of the pigment was assessed by cyclic voltammetry (Fig. 5), which measurements exhibited an anodic contribution at 0.5 V at the first potential scan. Interestingly, the anodic peak disappeared in the second swept, a known process that has been attributed to the electrode coating by the electroactive compound of the first scan [10]. On the other hand, an initial cathodic peak was observed at −0.52 V. In this case, the cathodic peak increased its intensity during the second and third swept, which can be attributed by an electrochemical compound produced in the anodic scan [10]. From our cyclic voltammetry results, prodigiosin showed an E_{HOMO} of 4.89 eV and an E_{LUMO} of 3.87 eV, corresponding to an energy band gap (E_g) of 1.02 eV. Using the band diagram with HOMO/LUMO prodigiosine levels shown in Fig. 5, it can be shown that this pigment meets the energy level required for use in a solar cell.

3.5. Dye-sensitized solar cell assembly

Prodigiosin immobilization on the TiO_2 film was measured spectrophotometrically. Results suggested that the maximum absorption of prodigiosin into the TiO_2 electrode was 0.57 mg mL^{-1} (Fig. 6a). Interestingly, the UV–Vis spectrum of the TiO_2/Prodigiosin anode exhibited a broader peak compared to the one obtained for prodigiosin in solution (Fig. 6b). Additionally, it showed a slight shift to higher wavelengths from 539 to 545 nm in a common phenomenon known as the bathochromic shift. This shift towards lower energy is known to be related to complexation reactions between functional anchoring groups of sensitizers and Ti^{4+} metal ions [41]. Particularly, the molecule of prodigiosin possesses three electron-donor pyrrolic nitrogens (Fig. 1b) capable of anchoring to the Ti^{4+} sites of TiO_2 by chelation [42], in addition to forming hydrogen bonds between the amine groups of the pigment and the oxygen atoms of the TiO_2 surface [43]. Furthermore, the rigid planar structure of pyrrolic rings might contribute to increase the proximity of the anchoring groups of the pigment to the surface of the TiO_2, favouring the binding process, which is related to the efficiency of photovoltaic conversion.

3.6. Evaluation of the performance of DSSC sensitized with prodigiosin

The evaluation of the performance of the prodigiosin-sensitized DSSC was carried out under standard conditions of solar illumination (1.5 a.m. 100 mW cm^{-2} light intensity). The results of the evaluation made evident the characteristic shape of the current-voltage curve and the time-dependent photographic response for the sensitized cell (Fig. 7a). On the other hand, the evaluation under complete darkness showed no photovoltage response during the studied time interval, as due to the negligible concentration of charge carriers in the valence band [24]. Meanwhile, the power curve obtained for the prodigiosin-sensitized DSSC (Fig. 7b), which provides the values of the maximum power of the solar cell, reached a power of 32 mW cm^{-2} when 0.39 V was applied.

Table 1 shows the electrical parameters obtained for the DSSC sensitized cell, which reached an efficiency of 0.032%, in comparison with the efficiency of 0.007% obtained from an untreated TiO_2 photoelectrode.

These results are comparable to those obtained by Órdenes-Aenishanslins et al. [23], who reported efficiencies of 0.0332% for DSSC sensitized with pigments isolated from the Antarctic bacteria *Hymenobacter* sp. and *Chryseobacterium* sp. (Table 2). However, it is noteworthy that these efficiencies were achieved at higher concentrations of the

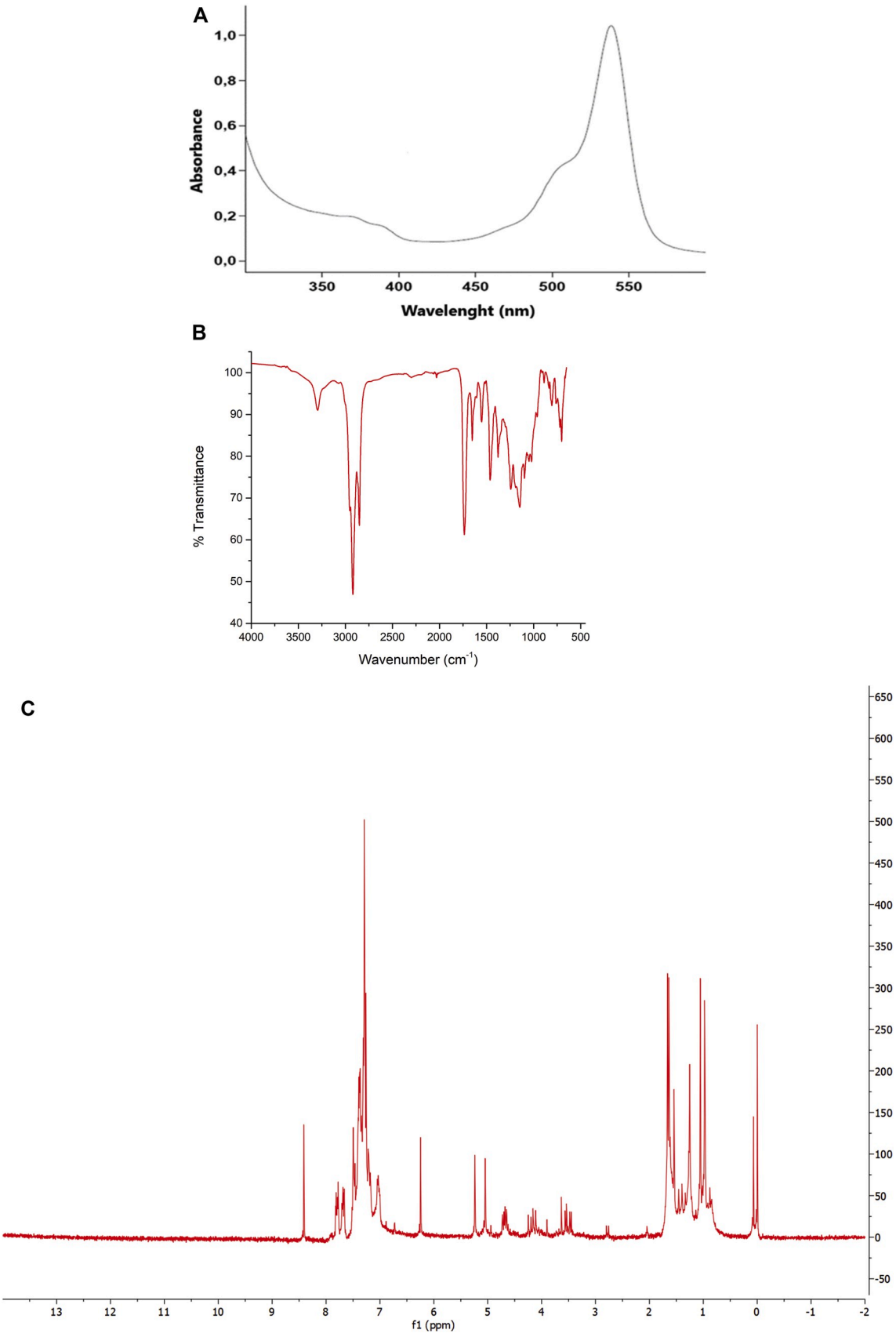

Fig. 3. (a) UV–Vis absorption spectrum; (b) Fourier-transform infrared spectrum; and (c) 1H NMR spectrum of the purified prodigiosin produced by *S. marcescens* 11E.

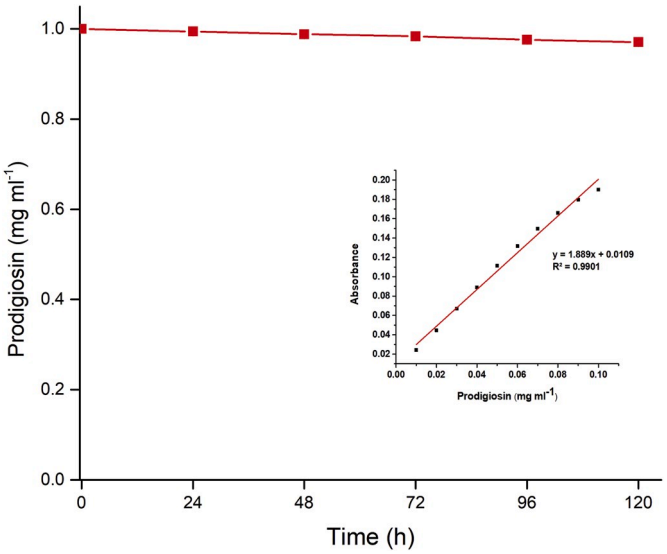

Fig. 4. Photostability evaluation and calibration curve of prodigiosin.

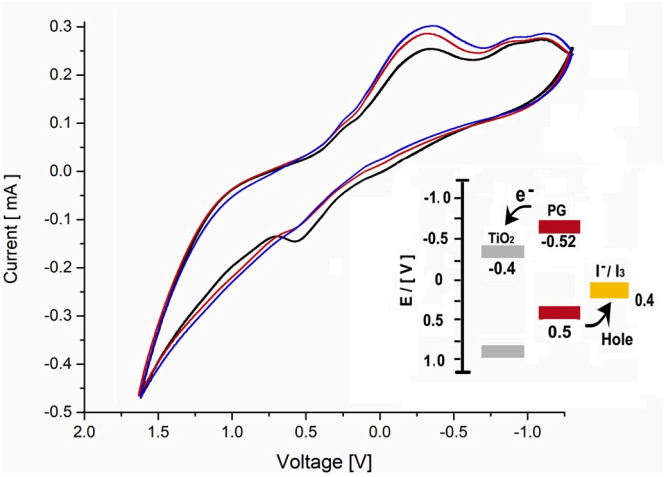

Fig. 5. Voltammetric profile of prodigiosin (black line: first scan, red line: second scan, blue line: third scan). Inset: energy level diagrams of the natural sensitizer showing the calculated position of HOMO/LUMO of prodigiosin (PG). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

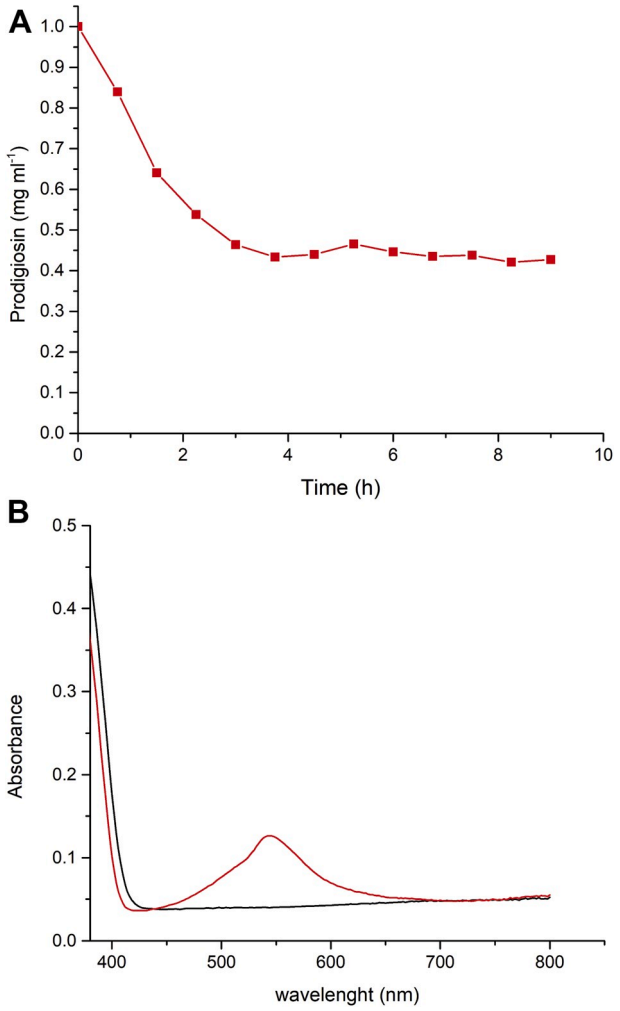

Fig. 6. (a) Prodigiosin immobilization on TiO_2 film (b), UV–Vis absorption spectrum of TiO_2/prodigiosin (red line) vs TiO_2 (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

pigments (10 mg mL^{-1}). Likewise, the parameters obtained in this work were higher than those reported for the pigment melanin extracted from the Antarctic bacterium *Streptomyces fildesensis, which* accomplished an efficiency of 0.014% using a concentration of 0.6 mg mL^{-1} of pigment [24]. Although other efforts have been made to identify bacterial pigments that could be used for the manufacture of DSSC [10], to date it has not been possible for these to reach efficiency levels that would allow them to compete against synthetic or plant-derived pigments [44].

Furthermore, it is essential to mention that studies reported in Table 2 were performed using Pt as a cathode or counter electrode. As platinized cathodes have low resistance and high catalytic activity for the I_2/I_3^- redox couple, it is used to collects electrons and catalyze oxide-reduction reactions. However, it is a scarce and expensive material [45]. Therefore, it is crucial to use alternative materials that can reduce the cost of production of DSSC. In this sense, the present work demonstrates that the use of economical material such as carbon can generate comparable responses in terms of photoelectrochemical parameters compared to those that use Pt.

From the electrochemical impedance spectroscopy measurements, a Nyquist plot was generated. This was used to propose a circuit scheme that could describe the electrochemical behaviour of the DSSC (Fig. 8, inset), which simulates a circuit with capacitance and resistance connected in parallel that represents the faradaic process and the double layer charging of the electrode interface. These elements are in a series circuit with the solution resistance. From the Nyquist plot several parameters of the DSSC can be described, such as the charge transfer resistance at the counter electrode (R_{CE}) and capacitance associated to the charge transfer in the counter electrode (C_{CE}); the charge transfer resistances at the interface of dye/TiO_2/electrolyte (R_{rec}), the chemical capacitance at the dye/TiO_2/electrolyte (Cμ) [46]. Finally, R_T corresponds to the transport resistance of the electron inside the nanostructured particles of the system (TiO_2/dye) [46].

The values of Cμ, R_{rec}, C_{CE}, R_{CE} and R_T obtained for prodigiosin-sensitized DSSC were 17 μF, and 8.4 KΩ, 23 μF, 158Ω and 242Ω respectively. The resulting high R_{rec} implies a slow charge recombination since larger resistance means a slower rate of recombination. Meanwhile, the value of R_{CE} was 260 Ω, which shows a high resistance for the charge transfer occurring at the counter electrode necessary for regeneration of the redox couple, affecting the overall conversion efficiency in the DSSC. The counter electrode in our DSSC was elaborated from carbon paste, thus the adsorption of molecules on the surface of the material could generate the high R_{CE} value in the electron transfer [10]. On the other hand, the recombination/transport ratio (R_{rec}/R_T)

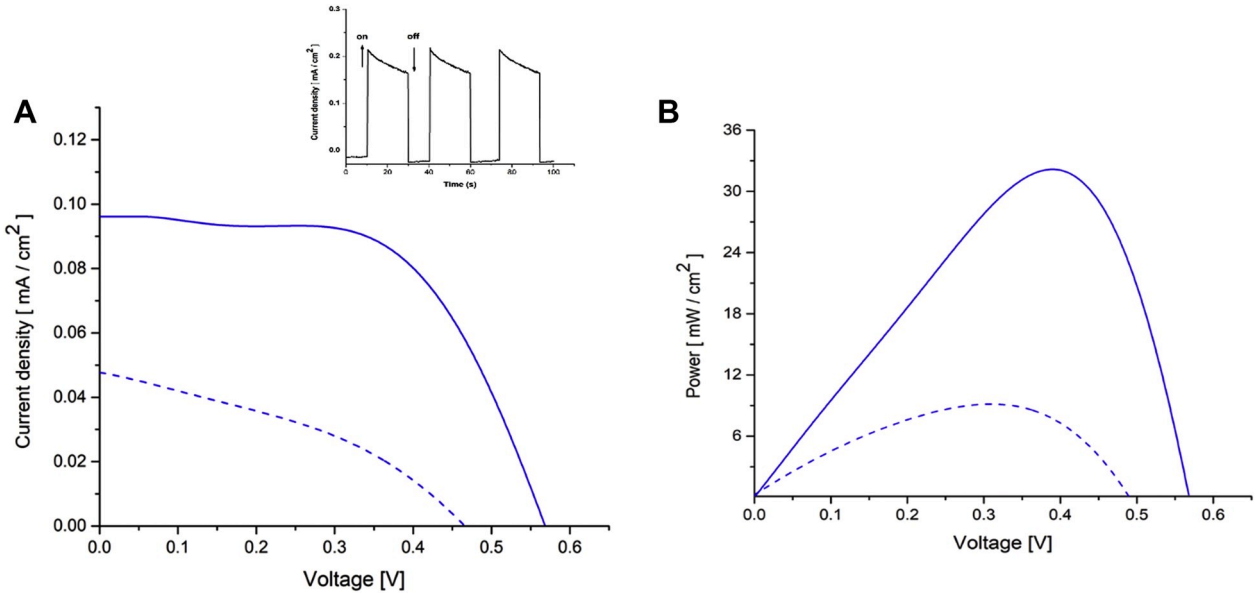

Fig. 7. (a) Photocurrent-voltage, and (b) power curves of the prodigiosin-sensitized DSSC (solid line) and untreated TiO_2 (dashed line).

Table 1
Photoelectrochemical parameters of the prodigiosin-sensitized DSSC.

Counter electrode	Photoelectrode	Short circuit current, *Jsc* [mA·cm^{-2}]	Open circuit voltage, *Voc* [mV]	Fill factor, FF (%)	Efficiency, ɳ (%)
Carbon	FTO/TiO_2/Prodigiosin	0.096 ± 0.018	560 ± 0.029	59.7 ± 0.68	0.032 ± 0.004
	FTO/TiO_2	0.048 ± 0.004	466 ± 0.006	31.0 ± 0.34	0.007 ± 0.001

Table 2
Photoelectrochemical parameters of DSSC fabricated with pigments extracted from bacteria.

Bacteria	Pigment	Short circuit current, *Jsc* [mA·cm^{-2}]	Open circuit voltage, *Voc* [mV]	Fill factor, FF (%)	Efficiency, ɳ (%)	Reference
Serratia marcescens 11E	Prodigiosin	0.096	560	59.7	0.032	This work
Hymenobacter sp.	Red	0.200	435	37.1	0.032	[23]
Chryseobacterium sp.	Yellow	0.130	548	48.4	0.032	[23]
Hymenobacter sp.	Orange	0.127	460	51.0	0.03	[10]
Streptomyces fildesensis	Melanin	0.051	419	57.0	0.014	[24]

indicates the time that takes for electrons to pass through TiO_2 [41]. The R_{rec}/R_T ratio obtained for our prodigiosin-sensitized DSSC was 34.7, which is considerably high in comparison with the ratio obtained for DSSCs sensitized with xanthophylls from *Hymenobacter* sp. (R_{rec}/R_T = 13) [10], and chlorophylls extracted from algae (R_{rec}/R_T = 1.25) [46], thus, indicating that the use of prodigiosin in the cell resulted in a lower electron loss.

The value τ ($\tau = R_{rec} \times C_\mu$) indicates the effective electron lifetime, which represents the time that takes for electrons to recombine from the conduction band to the valence band [46]. The recombination process observed in the prodigiosin-sensitized DSSC took around 0.14 s, while in a similar DSSC sensitized with a mixture of xanthophylls pigments extracted from *Hymenobacter* sp. UV11, the value τ was 0.032 s [10], demonstrating that prodigiosin have greater capacity to accumulate charges before recombining.

4. Conclusions

In this work, the use of the bacterial pigment prodigiosin as photosensitizers in solar cells is reported for the first time. Our results suggest that prodigiosin could be considered an excellent candidate to be used as a sensitizer for DSSC since the bacterial pigment exhibited a high degree of photostability, with a competitive efficiency compared to other bacterial pigments. Besides, taking into account that overproduction of prodigiosin can be easily achieved on a large scale through the rapid fermentation of agro-industrial residues throughout the year, which would avoid serious ecological problems as deforestation and infringement to the diversity of local species, this study illustrates the feasibility to use bacterial pigments for their application in the development of a low-tech and low-cost DSSC.

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.

CRediT authorship contribution statement

Patricia Hernández-Velasco: Investigation. **Irene Morales-**

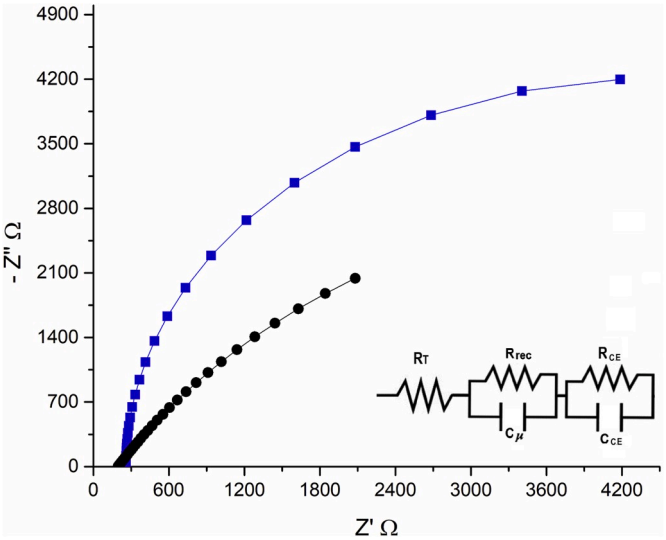

Fig. 8. Nyquist plot of the circuit scheme used to describe the electrochemical behaviour of the prodigiosin-sensitized DSSC (blue line) and the non-sensitized DSSC (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Atilano: Investigation. **Melissa Rodríguez-Delgado:** Funding acquisition, Supervision, Formal analysis. **José Manuel Rodríguez-Delgado:** Validation, Investigation, Formal analysis. **Donato Luna-Moreno:** Resources, Formal analysis. **Francisco Guadalupe Ávalos-Alanís:** Resources, Formal analysis. **Juan Francisco Villarreal-Chiu:** Conceptualization, Writing - review & editing.

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