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Review

Peptide Materials in Dye Sensitized Solar Cells

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Abstract: In September 2015, the ONU approved the Global Agenda for Sustainable Development, by which all countries of the world are mobilized to adopt a set of goals to be achieved by 2030. Within these goals, the aim of having a responsible production and consumption, as well as taking climate action, made is necessary to design new eco-friendly materials. Another important UN goal is the possibility for all the countries in the world to access affordable energy. The most promising and renewable energy source is solar energy. Current solar cells use non-biodegradable substrates, which generally contribute to environmental pollution at the end of their life cycles. Therefore, the production of green and biodegradable electronic devices is a great challenge, prompted by the need to find sustainable alternatives to the current materials, particularly in the field of dye-sensitized solar cells. Within the green alternatives, biopolymers extracted from biomass, such as polysaccharides and proteins, represent the most promising materials in view of a circular economy perspective. In particular, peptides, due to their stability, good self-assembly properties, and ease of functionalization, may be good candidates for the creation of dye sensitized solar cell (DSSC) technology. This work shows an overview of the use of peptides in DSSC. Peptides, due to their unique self-assembling properties, have been used both as dyes (mimicking natural photosynthesis) and as templating materials for TiO_2 morphology. We are just at the beginning of the exploitation of these promising biomolecules, and a great deal of work remains to be done.

Keywords: peptide; solar energy; sustainability; dye sensitized solar cell

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1. Introduction

In September 2015, the UN approved the Global Agenda for Sustainable Development, by which all countries of the world are mobilized to adopt a set of goals to be achieved by 2030. One of these goals is to ensure access to affordable, reliable, and sustainable energy for all the countries in the world. In order to do this, the transition from the currently used health-damaging cook stoves to the use of renewable energy sources should be accelerated. Within the renewable energy sources, solar energy has the greatest potential [1–5]. Each day, the sun radiates 165,000 TW of power to the face of the Earth, which may be exploited to produce electricity in a "economical" way. For this reason, in recent years, dye-sensitized solar cells (DSSCs) have gained widespread attention, thanks to their low production cost, ease of manufacture, and tunable optical properties. These optical properties include the possibility of color selection, while still assuring transparency, a low dependence of their performance on the light angle, a better response in diffuse light compared to semiconductors-based PV technologies, and environmental sustainability [6–14]. In DSSC technology, a dye captures the sunlight in a manner similar to the capture of sunlight in natural photosynthesis, producing an electron injection into the conduction band of a metal oxide, giving rise to charge separation. The schematic assembly of a DSSC is reported in Figure 1A, while the schematic principle of operation is reported in Figure 1B. The first paper using this technology employed ruthenium-based dyes in combination with iodide-based electrolyte [6]. By using a porphyrin dye, molecularly engineered to attain the archetypal structure of a donor-π-bridge-acceptor, and a cobalt (II/III) redox couple, an efficiency of more than 13% (certified value) was achieved [15,16]. Recently, the efficiency has reached 14% (non-certified) by using co-sensitized organic dyes [17,18]. These values, however, are still less than those offered by first- and second-generation solar cells, i.e., thin-film solar cells and Si-based solar cells which offer an efficiency of ~20–30% [10,19–21]. Under indoor light, DSSC exhibits all its potential, with efficiencies above 34% [17,22–25]. The DSSC improvement in technology efficiency was achieved by focusing on the different materials and related processes forming the cell: nanostructured metal oxide electrodes [18,26–31], sensitizers [15,17,32–34], charge transport materials [35,36], and counter electrodes [37].

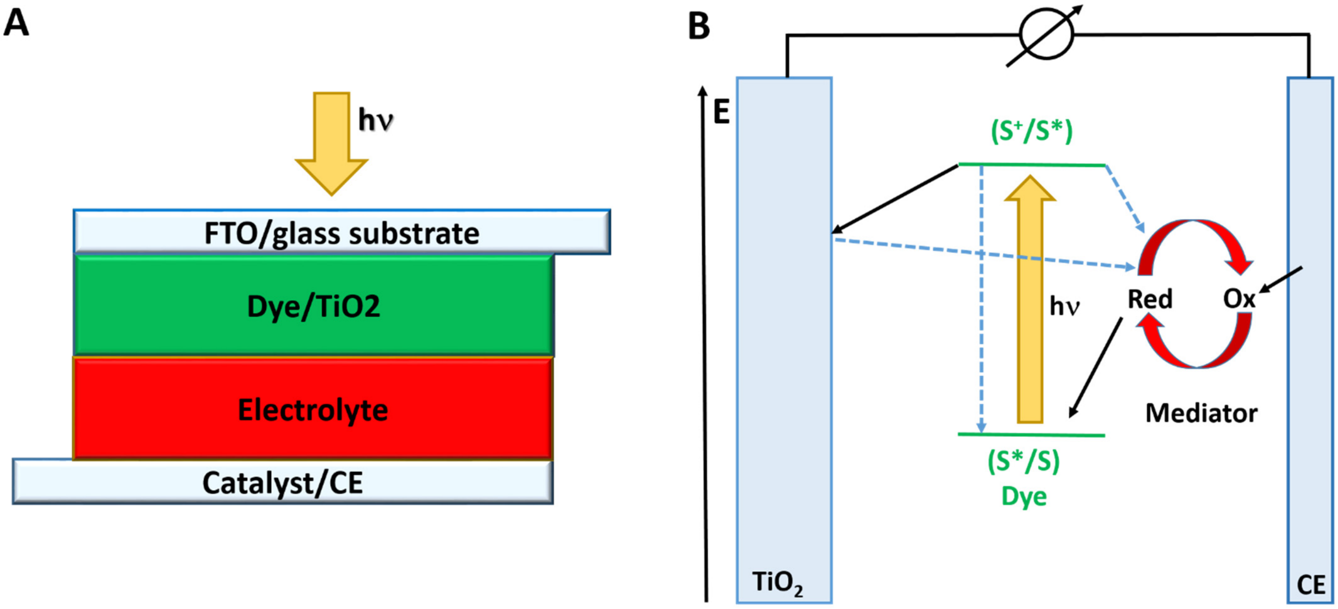

Figure 1. (**A**) The schematic structure and (**B**) main processes and principles of operation of the dye-sensitized solar cell.

The industrialization and commercialization of DSSC technology is feasible if the small-area lab cells are scaled-up to the module (e.g., connection of different cells) and panel (e.g., connection of different modules) [35,36] size. This complicates the manufacturing, performance, and stability, with respect to the lab cells [37].

Currently, however, the introduction of perovskite solar cells (PSCs) [38–41], the innovative lead-based technology that has rapidly and meaningfully exceeded the DSSC efficiencies by a factor of two in both flexible and rigid devices [22], surpassed the effective role and prospects of DSSCs for utility-scale solar energy uses. The fabrication procedures, comparable with those of organic electronics and dye-sensitized solar cells, have driven their success in terms of the performance of PSC technology [42]. On the other hand, at present, the stability and toxicity of perovskite materials remain inspiring issues; thus, DSSCs and other emergent photovoltaic technologies should be developed in order to offer the possibility to advance solar cells due to their color, transparency, large flexibility, and tandem configuration [43].

Scientists have developed very innovative materials focusing on the long-term stability and high efficiency of solar cells, while often setting aside the concept of sustainability. However, in light of the effective industrialization of this technology, sustainability should be taken into consideration as an necessary keyword [44]. At the present time, DSSCs are finding a “new way back” to sustainability, since many reports have focused on the preparation of green and economical materials to replace the standard substances [13,45–48]. Moreover, the possibility of using recycled materials has been exploited [49,50]. Besides the improvement in performance, scientists have also modified all the DSSC components, i.e., the sensitizer, the electrolyte, the redox couple, and the counter electrode, in order to realize more economical, eco-friendly and sustainable next-generation solar cells, in accordance with the inspiring idea that Grätzel first aimed to achieve [6].

The best way to maintain system efficiency and build sustainable materials is to take inspiration from nature. Biomimetic photovoltaic solar cells have attracted great interest during the last few decades and have shown remarkable enhancements in power conversion efficiency [51].

As a matter of fact, natural selection is the main mechanism of evolution, selecting optimal characteristics for the survival of an organism. For this reason, using the same building blocks used by nature to create novel materials can be a very helpful solution in solving engineering problems, while at the same time, assuring material sustainability. In particular, in nature, all the electron transfer (ET) processes occur efficiently along a consecutive arrangement of redox groups inserted in polypeptide matrices [52,53]. These polypeptide media are generally supposed to assume the role of scaffolds to fix the three- dimensional position of the redox groups, but also of mediators to facilitate ET. The α-helix is the most recurrent secondary structure found in these matrices, and it is believed to play a central role in the good efficiency found in the naturally occurring electron transfer process [54]. For ET reactions through model α-helical peptides, a tunnelling factor of 0.66 $Å^{-1}$ has been reported, which is considerably smaller than that obtained in alkyl chains, confirming that helical peptides are a proper matrix for electron transfer [55]. Furthermore, the macrodipole moment obtained from the vector sum of the individual peptide dipoles in the α-helical secondary structure generates an intrinsically polar macromolecule (Figure 2), which has been demonstrated to notably accelerate ET reactions in the same direction of the generated electric field, both in the solution [56,57] and on the surface [58].

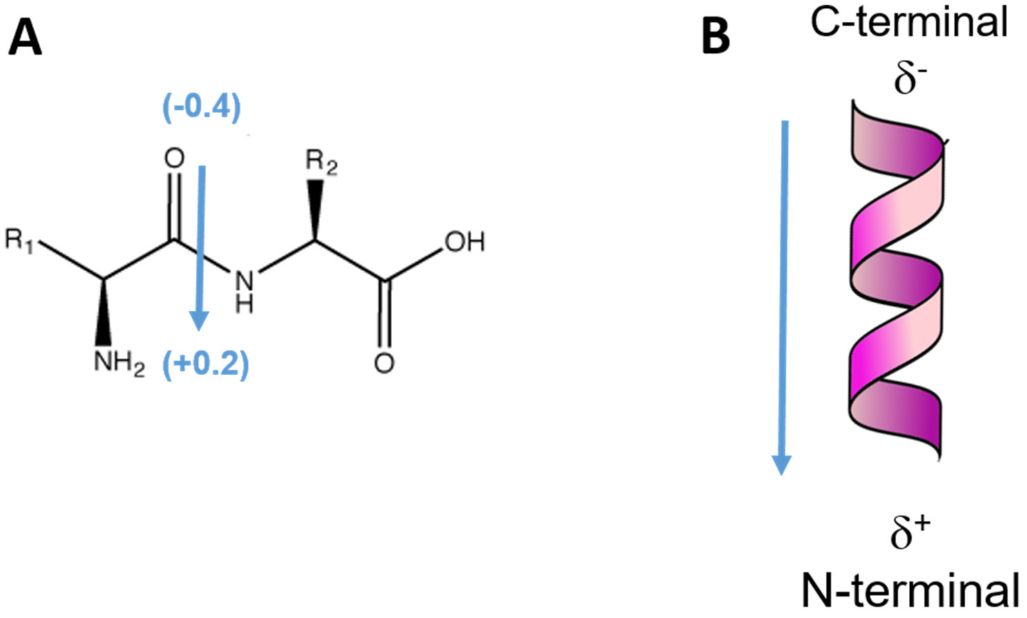

Figure 2. (**A**) Dipole moment of the peptide bond and (**B**) alignment of all the dipoles along the helix axis in a helical conformation.

During our studies, we have demonstrated that the 3_{10}-helix secondary structure also has the same rectifying property, both in the solution [59] and on the surface [60–62], but to a lesser degree than that of the α-helix, due to the hydrogen bond distortion along the helix in the former structure [63].

Although the tunnelling factor of helical peptides is larger than those of other macromolecules, such as phenylene-ethynylene [64,65] or phenylene-vinylene [66,67], helical peptides have several advantages for the development of practical molecular electronic components in terms of well-specified molecular structure, facile molecular design, robustness, biocompatibility, and arrangement of functional groups along the molecule. Furthermore, helical peptides have peculiar self-assembling properties, which can be suitably exploited in the building up of nanostructures, and fundamentally, peptides can be extracted from natural sources, in order to realize a new generation of green solar cells based on renewable components. In this prospective article, we provide a description of the most significant and recent advances in solar energy conversion strategies using peptides. This review highlights the key advantages of using peptides in DSSC, both as a templating matrix for light-harvesting dyes and as templating materials to obtain different TiO_2 nanostructures.

2. Peptides as Dyes

In natural photosynthesis, plants use lipoproteins as templates to sort chlorophyll dyes in an ideal arrangement, in order to confer directionality to the ET process and reduce strong interactions between different molecules.

One of the approaches used by scientists in order to follow the teachings of nature is the immobilization of photosynthetic proteins on gold and TiO_2 surfaces. Photosynthetic proteins and Photosystems I and II, have been effectively used as bioinspired devices for photoinduced electric current generation [68–73], but their low stability, once they venture far from their natural environment, strictly restricts their use. The possibility of enhancing protein stability was exploited using bacteriorhodopsin, a thermally stable protein activated by light [74].

Another approach uses self-assembled monolayers of helical peptides as encouraging materials for very efficient current generation under light [60–62,75–84]. By using peptides, it is possible to maintain all the advantages of protein materials (templating properties, capability of the electrons to be transferred over long lengths, the ability to impede charge recombination), in addition to their capability to precisely auto-organize on the surface, creating an oriented two-dimensional array. This assures ET directionality and increments the molecular density on the surface. Over the years, several studies have explored ET processes in 2D self-assembled monolayers (SAMs) bound to a gold surface by changing the peptide length, conformation, and sequence. In particular, it has been demonstrated that the peptide length influences the electron transfer rate constant and the SAM surface density. Long peptides (with at least 12 residues) attain helical conformations, while shorter peptides have disordered secondary structures, which avoid the formation of a stable self-assembled monolayer. However, the ET rate constant improves by reducing the chain length, that is, by reducing the distance between the dye and the surface. It has been demonstrated that using conformationally constrained amino-acids, which are residues with a double substitution on the C^{α}, as well as very short peptides containing only six residues, may help to attain helical conformations [60,79–84]. In this way, it is possible to have a compact SAM, where peptides attain a helical conformation, and in which the dye is quite close to the surface, thereby assuring a good ET efficiency of the system. In a further study, by exploiting the helix dipole–dipole interaction, it has been demonstrated that it was possible to use peptides as building blocks, similar to a "LEGO" set. In particular, we succeeded in the insertion of a peptide, devoid of the sulphur group, into an SAM, just by exploiting non-covalent interactions [61].

Recently, the "LEGO kit" was implemented, by introducing not only a peptide able to laterally interact with the peptides already linked to the gold surface, thereby improving the SAM compactness, but also by the realization of a 3D supramolecular structure on the surface, where the film length may be controlled by head-to-tail interactions between molecules containing the thymine and adenine moieties at the extremities (Figure 3) [85,86]. Interestingly, it has been found that the efficiency of the photocurrent generation process was influenced by the helical secondary structure attained by the peptide, which was modulated by the pH. In particular, the α-helix (obtained at pH 11) was found to be more efficient than the 3_{10}-helix (found at pH 4) [86]. This innovative approach allowed for the control of the three-dimensional (3D) organization of molecules on surfaces, so as to confer molecular order and the perfect positioning of different redox centers, which is a fundamental aspect for the design of artificial photosynthetic systems in order to control the direction of electronic flow [55–58,63,87].

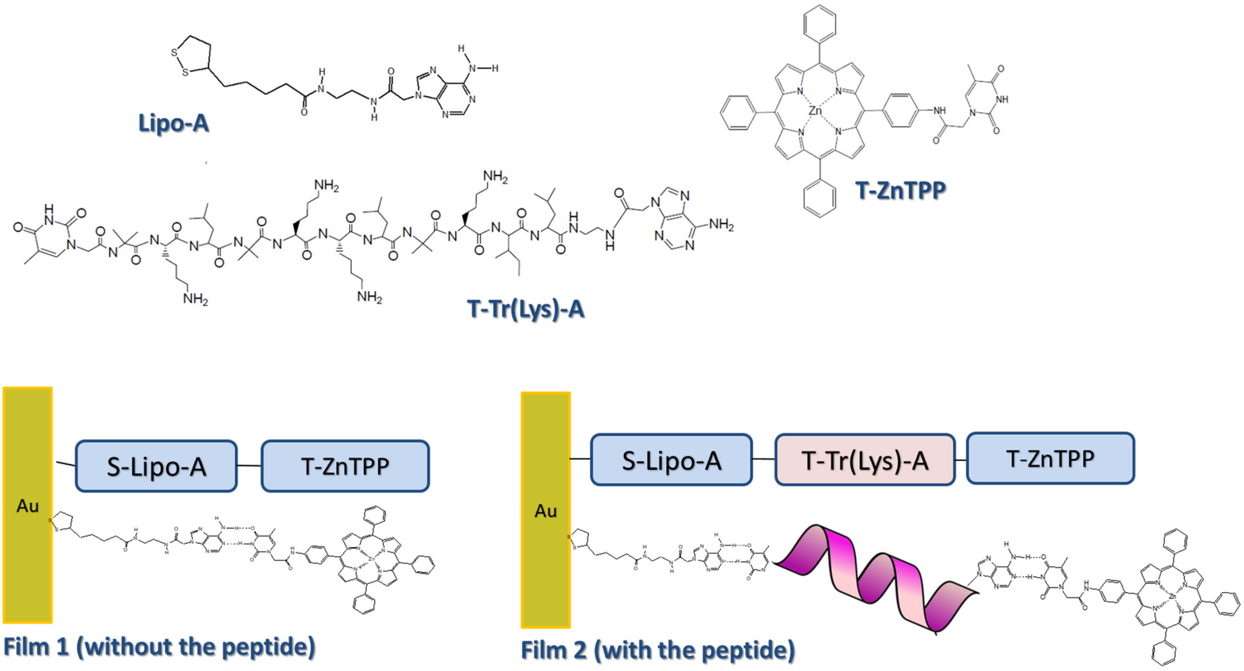

Figure 3. Chemical structures of the building blocks used for the construction of films reported in ref. [85].

However, despite fundamental achievements in the field, very few results concerning peptide-based DSSC have so far been reported in the literature. In particular, as already reported, in nature, ET processes occur in photosynthetic proteins, which are predominantly in helical conformations. It has been demonstrated that the helix is fundamental to make ET possible over long distances (>10 Å). Furthermore, the large electric dipole moment (about 3.6 D per residue) associated with a helical conformation makes the system behave as a molecular photodiode, accelerating ET in the same direction of the dipole-generated electric field, and inhibiting charge recombination [75]. Recently, trying to mimic this natural process, a peptide-based dye sensitized solar cell (DSSC) was built: a helical hexapeptide, able to self-organize on the surface in an ordered manner, has been able to create an oriented two-dimensional array, conferring rectifying properties to the surface (Figure 4) [88]. Despite the fact that the peptide used had dye absorbing capabilities only in the UV region, and despite the use of a non-standard water-based electrolyte, this system was able to improve the photoconversion efficiency of the only dye by 10 times. Moreover, the system was stable after several cycles of measurement.

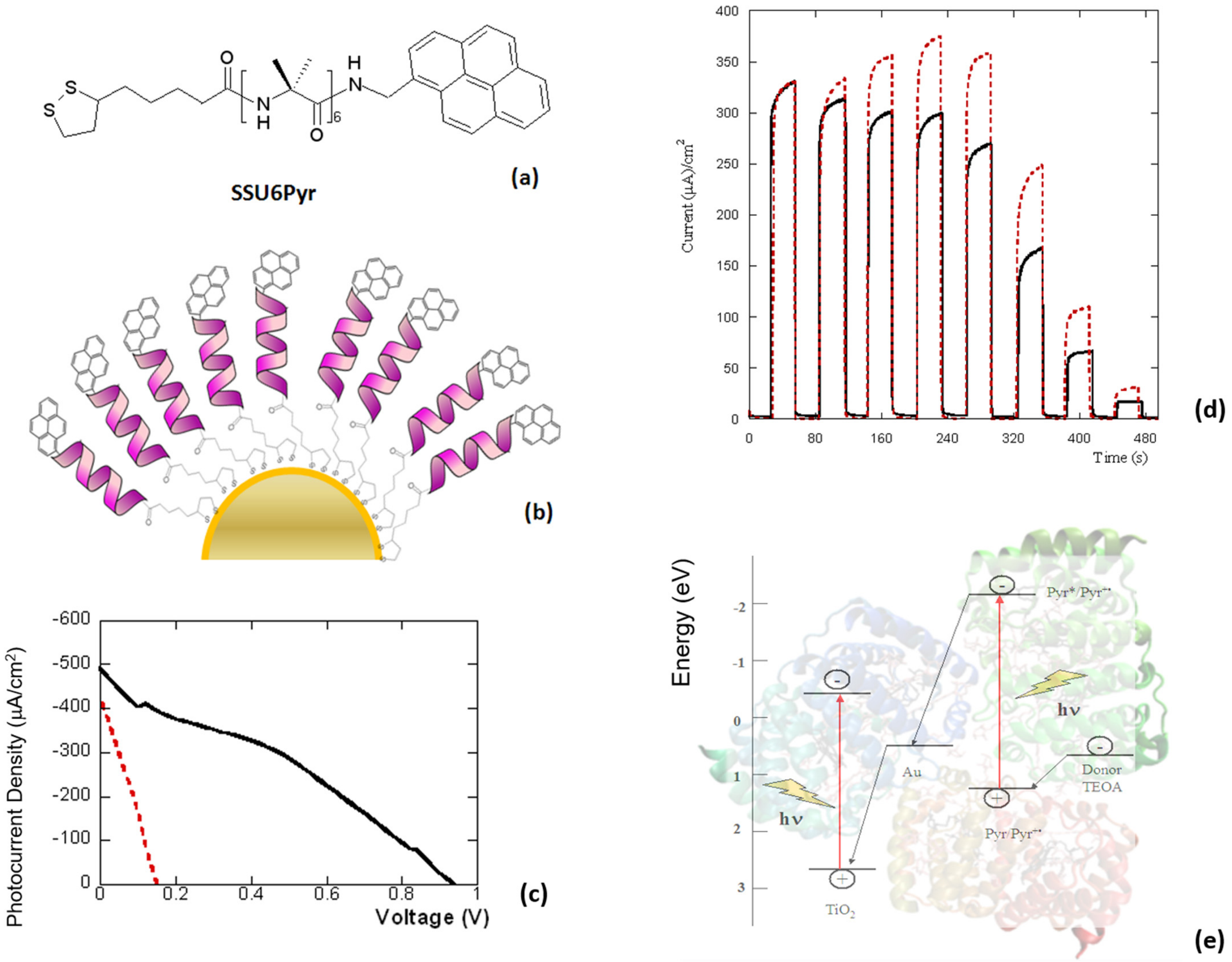

Figure 4. (**a**) Chemical formula and acronym of the peptide investigated in the work of the authors of [88]. (**b**) Schematic representation of the peptide on the gold-covered TiO_2 nanostructured surface. (**c**) Photocurrent vs. voltage behavior of the peptide-based cell (black solid curve). The photoresponse of the Au/TiO_2/FTO electrode is also reported for comparison (red dotted line). (**d**) Time course of the photocurrent generated by the SSU6Pyr film on the Au/TiO_2/FTO electrode (dotted red line) as compared to the bare Au/TiO_2/FTO electrode (continuous black line) and to the pyrene chromophore adsorbed on the Au/TiO_2/FTO electrode (dashed grey line). The measurements have been performed in aqueous TEOA solution, at 0 V vs. Ag/AgCl, upon photoirradiation at different wavelengths (every 10 nm from 320 to 390 nm). (**e**) Schematic representation of the energy levels involved in the photocurrent process. Reproduced with permission from ref. [88], copyright Wiley.

In another study, a dodecapeptide was synthesized (TAMRA-AMRKLPDAPGMH, acronym: T12) containing a specific binding sequence, namely the hexapeptide motif RKLPDA, which is able to bind to the TiO_2 surface [89]. The peptide was functionalized with a tetramethylrhodamine dye. Photocurrent generation experiments were therefore performed to determine the photon-to-current conversion efficiency (IPCE) of a DSSC, of which the photoactive component was composed of TAMRA-AMRKLPDAPGMH/TiO_2 (Figure 5). The obtained IPCE was 0.65%, a value that is certainly quite low, but is, in any case, higher than those previously reported for similar bioinspired DSSCs. These results point out that peptide scaffolds can be considered as encouraging materials for the design of molecular building blocks to be used in DSSCs.

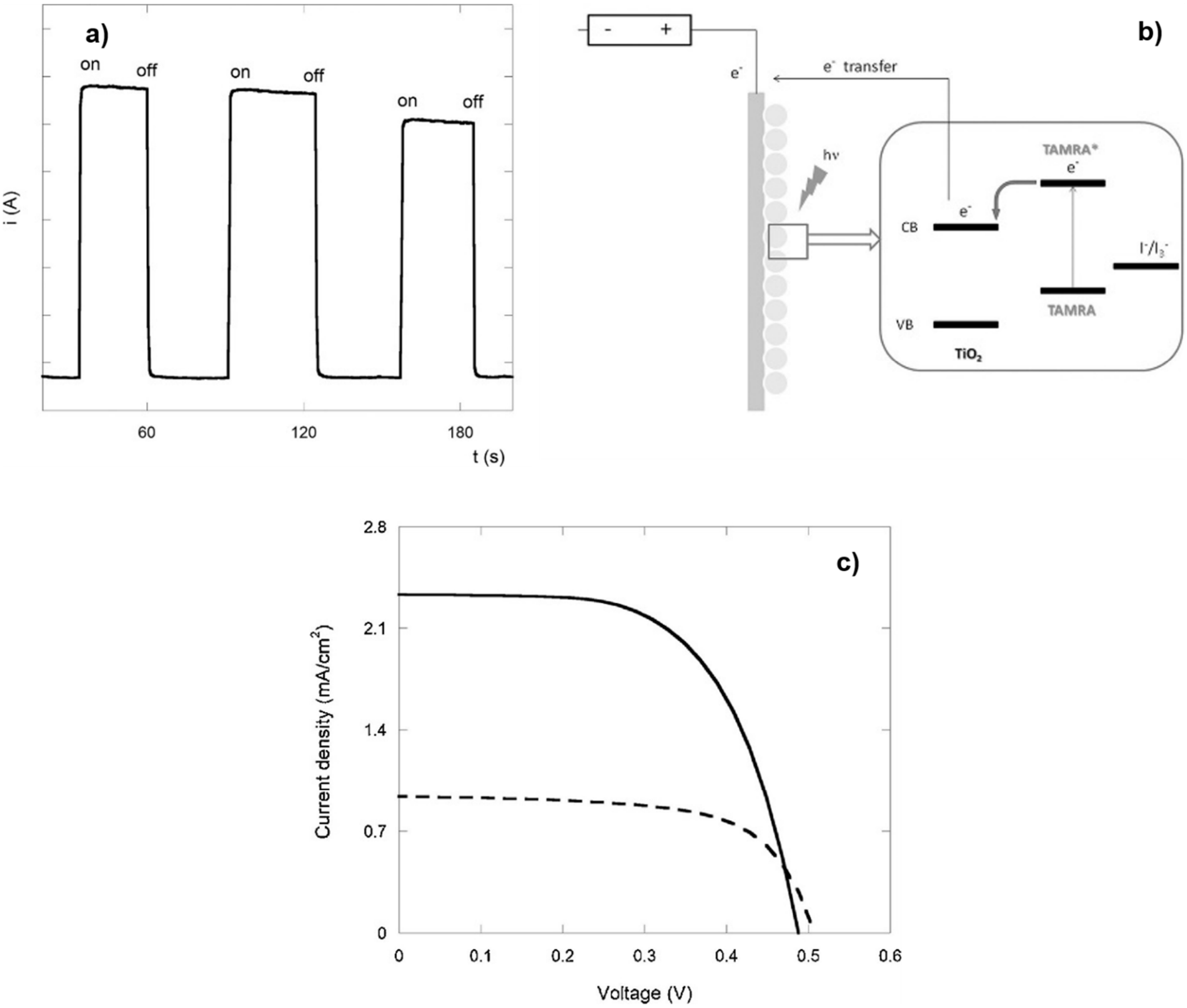

Figure 5. Photocurrent generation experiments performed on the T12 peptide immobilized on a TiO_2/FTO electrode. (**a**) Photocurrent on-off graphic at 0 V bias potential, under illumination at λ = 550, 560, and 570 nm. (**b**) Scheme of the energy states and of the electron transfer flow responsible for the photocurrent process. (**c**) I-V characteristics of the T12/TiO_2/FTO electrode (continuous line) and of the bare TiO_2/FTO electrode (dotted line). Adapted from ref. [89], with permission from Elsevier.

All these results demonstrate that conformationally constrained peptides are good candidates for solar cell technology, paving the way for the use of peptides extracted from plants or algae in a new generation of green solar cells based on renewable components.

3. Peptides as Templating Materials

Another important application of peptides into DSSC is the possibility of using them as templating materials. In order to enhance the efficiency of DSSCs, several parameters should be controlled, including the physicochemical properties of the TiO_2 components. In particular, a larger surface area for better dye adsorption, greater pore volumes and diameters, hole conduction efficiency, and a network of individual nano-structures are crucial in a DSSC [90,91]. Conversely, the application of TiO_2 nanoparticles in DSSCs causes electron trapping in the nanostructured film, limiting the power conversion efficiency of these devices. The time scale for injection and carrying of the electrons by TiO_2 is similar to the time scale of charge recombination by the electrolyte [92]. The competition between these time scales fixes the photon-to-current conversion efficiency of the DSSC. The principal problem of DSSCs is the loss of electrons at the TiO_2–electrolyte interface. It has been demonstrated that charge transport through a one-dimensional TiO_2 nanostructures is easier because this structure causes minor resistance to diffusion [93].

One-dimensional titania nanostructures give rise to an enhancement in the short circuit current (J_{sc}) and open circuit voltage (V_{oc}), since when they are used as a support for light absorbing molecules, they are able to transport electrons before the recombination process takes place. The possibility of using self-assembled nanofibers of amyloid-like peptides as an organic template able to favor the growth of one-dimensional TiO_2 nanostructures can promote an eco-friendly strategy to build this kind of anodic materials in DSSCs [94,95]. In general, the peptide used for this kind of application is diphenylalanine (FF). FF is a well-known structural motif for the β-amyloid, associated with Alzheimer's disease, giving rise to supramolecular peptide nanotubes [96]. By combining peptide self-assembly and the atomic layer deposition technique (ALD), Kim et al. fabricated an empty TiO_2 nanoribbon network using a biotemplating process [94]. First, the peptide was self-assembled onto the surface, and then a thin TiO_2 layer was deposited at the surface of the peptide template via ALD. After the pyrolysis of the peptide template, a nanotubular TiO_2 framework was successfully prepared. It was also possible to control the evolution of the crystal phase and crystallite size of the TiO_2 nanostructure by controlling the calcination temperature. The authors integrated a hollow TiO_2 nanoribbon network electrode into a DSSC device, and they discovered that the photo-electrochemical performance of this cell showed a power conversion efficiency of 3.8%, which is comparable to a conventional TiO_2 nanoparticle-based DSSC (3.5%). Interestingly, the aromatic peptide self-assembly exhibits high thermal stability, allowing a fine temperature control of the process, and thus the possibility to apply conventional vacuum deposition techniques.

A similar methodology was followed by Guler et al., exploiting two de novo designed hexapeptides, with high binding affinity to metal ions, for the synthesis of nanostructured TiO_2 [95]. Both peptides have an FF group to favor aggregation, but differ for the N- and C-terminal residues, being a lysine (K) residue in peptide 1 (P1, Figure 6a, Ac-KFFAAK) and a glutamate (E) residue in peptide 2 (P2, Figure 6b, Ac-EFFAAE). These terminal groups act as nucleation and growth centers for TiO_2. Owing to the long side chains of the K residues, P1 is longer than P2 (Figure 6a,b). For this reason, the self-assembled peptide nanofibers formed by P1, having an average diameter of 11.4 ± 0.4 nm, are slightly thicker than the ones formed by P2 (Figure 7a,b), which showed an average diameter of 9.1 ± 0.6 nm. Interestingly, this small difference strongly affects the morphology of TiO_2 nanostructures. P1 was found to template the growth of a nanotubular TiO_2 structure, while P2 favored a TiO_2 nanowire architecture (Figure 7a,b). To understand the effect of the morphology of TiO_2 nanostructures morphology on the DSSC performance, three samples were studied: P1-templated TiO_2, P2-templated TiO_2, and template-free synthesized TiO_2. It has been shown that the K residues in P1 prevented the complete sintering of the material into nanowires during the calcination process, giving rise to nanotubular structures. These structures were characterized by a surface area that was, respectively, five and three times higher than the surface area of the template-free TiO_2 nanoparticles. The J–V curves showed that the nanostructured devices exhibited higher photovoltaic performance. In particular, P1 nanotubes (efficiency 0.83%) were definitely more efficient than the nanowire structures obtained with P2 (efficiency 0.44%), and both showed higher efficiencies than the template-free substrate (efficiency 0.27%).

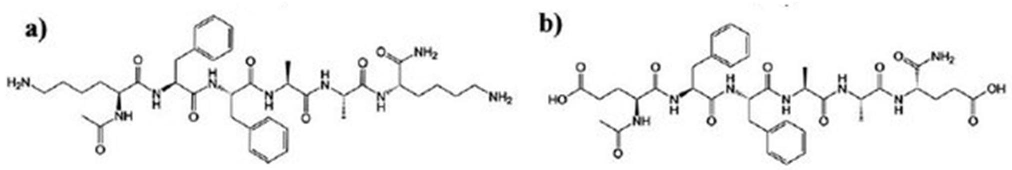

Figure 6. Molecular structure of P1 (**a**) and P2 (**b**) peptides reported in [95], with permission from the Royal Society of Chemistry.

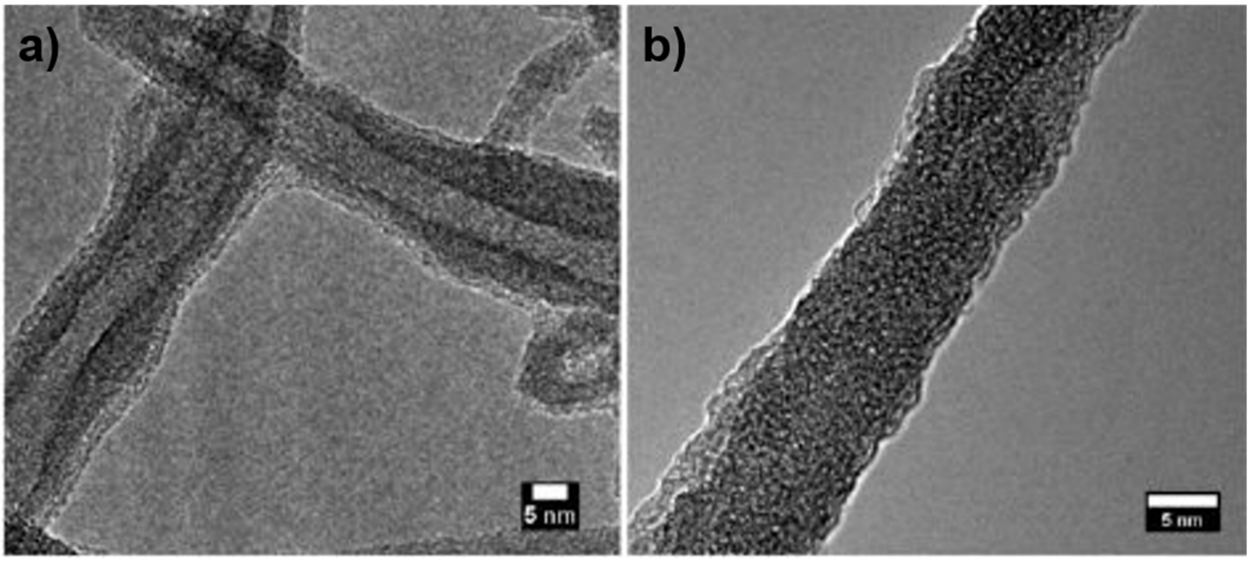

Figure 7. TEM images of P1-templated TiO_2 nanotubes (**a**) and P2-templated TiO_2 nanowires (**b**) obtained after calcination, adapted from [95], with permission of the Royal Society of Chemistry.

4. Conclusions and Future Directions

In conclusion, in this review, we have discussed the function of peptides as sustainable materials in DSSC. In particular, we have learned about the possibility of using peptides as bridges between a dye and the electrode surface, such use favoring the photo-induced electron transfer process in one specific direction and avoiding charge recombination. This photodiode-like capability improves the process efficiency, making peptide-based DSSC very promising.

Secondly, peptides can also be used as templating materials due to their abilities to self-assemble in a fascinating and ordered way. Different peptides may give rise to different supramolecular structures, modulating the properties of the TiO_2 film obtained. In the future, the possibility of using peptides extracted from natural sources may improve both the production capability and the economic and environmental sustainability of the process.

Due to their biodegradability and biocompatibility, peptides are a new class of materials that can help to heal the future of our planet.

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References

1. Beller, M.; Centi, G.; Sun, L. Chemistry Future: Priorities and Opportunities from the Sustainability Perspective. *ChemSusChem* **2017**, *10*, 6–13. [CrossRef] [PubMed]
2. Su, D.S. (Ed.) Special Issue: Energy Conversion and Storage. *ChemSusChem* **2012**, *5*, 441–599.
3. Gong, J.; Li, C.; Wasielewski, M.R. Advances in solar energy conversion. *Chem. Soc. Rev.* **2019**, *48*, 1862–1864. [CrossRef] [PubMed]
4. Crabtree, G.W.; Lewis, N.S. Solar energy conversion. *Phys. Today* **2007**, *60*, 37–42. [CrossRef]
5. Ginley, D.; Green, M.A.; Collins, R. Solar Energy Conversion toward 1 Terawatt. *MRS Bull.* **2011**, *33*, 355–364. [CrossRef]
6. O'Regan, B.; Grätzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films. *Nature* **1991**, *353*, 737–740. [CrossRef]
7. Kalyanasundaram, K. *Dye-Sensitized Solar Cells*; EPFL Press: Lausanne, Switzerland, 2010.
8. Nath, N.C.D.; Lee, J.J. Binary redox electrolytes used in dye-sensitized solar cells. *J. Ind. Eng. Chem.* **2019**, *78*, 53–65. [CrossRef]
9. Ye, M.; Wen, X.; Wang, M.; Iocozzia, J.; Zhang, N.; Lin, C.; Lin, Z. Recent advances in dye-sensitized solar cells: From photoanodes, sensitizers and electrolytes to counter electrodes. *Mater. Today* **2015**, *18*, 155–162. [CrossRef]
10. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-sensitized solar cells. *Chem. Rev.* **2010**, *110*, 6595–6663. [CrossRef]
11. Khanna, S.; Sundaram, S.; Reddy, K.S.; Mallick, T.K. Performance analysis of perovskite and dye-sensitized solar cells under varying operating conditions and comparison with monocrystalline silicon cell. *Appl. Therm. Eng.* **2017**, *127*, 559–565. [CrossRef]
12. Dominici, L.; Vesce, L.; Colonna, D.; Michelotti, F.; Brown, T.M.; Reale, A.; Di Carlo, A. Angular and prism coupling refractive enhancement in dye solar cells. *Appl. Phys. Lett.* **2010**, *96*, 13302. [CrossRef]
13. Parisi, M.L.; Maranghi, S.; Vesce, L.; Sinicropi, A.; Di Carlo, A.; Basosi, R. Prospective life cycle assessment of third-generation photovoltaics at the pre-industrial scale: A long-term scenario approach. *Renew. Sustain. Energy Rev.* **2020**, *121*, 109703. [CrossRef]
14. Borella, L.; Vesce, L.; Mariani, P.; Barichello, J.; Di Carlo, A.; Trivellin, N.; Sforza, E. Spectral changes by dye sensitized solar modules influence the pigment composition and productivity of arthrospira maxima and increase the overall energy efficiency. *Adv. Sustain. Syst.* **2022**, *6*, 2100346. [CrossRef]
15. Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B.F.E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M.K.; Grätzel, M. Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers. *Nat. Chem.* **2014**, *6*, 242–247. [CrossRef] [PubMed]
16. Zhang, D.; Stojanovic, M.; Ren, Y.; Cao, Y.; Eickemeyer, F.T.; Socie, E.; Vlachopoulos, N.; Moser, J.-E.; Zakeeruddin, S.M.; Hagfeldt, A.; et al. A molecular photosensitizer achieves a V_{oc} of 1.24 V enabling highly efficient and stable dye-sensitized solar cells with copper(II/I)-based electrolyte. *Nat. Commun.* **2021**, *12*, 1777. [CrossRef] [PubMed]
17. Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.-I.; Hanaya, M. Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes. *Chem. Commun.* **2015**, *51*, 15894–15897. [CrossRef]
18. Ji, J.-M.; Zhou, H.; Eom, Y.K.; Kim, C.H.; Kim, H.K. 14.2% Efficiency Dye-Sensitized Solar Cells by Co-sensitizing Novel Thieno[3,2-*b*]indole-Based Organic Dyes with a Promising Porphyrin Sensitizer. *Adv. Energy Mater.* **2020**, *10*, 2000124. [CrossRef]
19. Sharma, K.; Sharma, V.; Sharma, S.S. Dye-Sensitized Solar Cells: Fundamentals and Current Status. *Nanoscale Res. Lett.* **2018**, *28*, 381–427. [CrossRef] [PubMed]
20. Hara, K.; Arakawa, H. *Handbook of Photovoltaic Science and Engineering*; Luque, A., Hegedus, S., Eds.; John Wiley & Sons, Ltd.: Hoboken, NJ, USA, 2003; pp. 663–700.
21. Green, M.A.; Dunlop, E.D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Hao, X. Solar cell efficiency tables (version 59). *Prog. Photovolt. Res. Appl.* **2022**, *30*, 3–12. [CrossRef]
22. Wan, J.; Tao, L.; Wang, B.; Zhang, J.; Wang, H.; Lund, P.D. A facile method to produce TiO_2 nanorods for high-efficiency dye solar cells. *J. Power Sources* **2019**, *438*, 227012. [CrossRef]
23. Zardetto, V.; De Angelis, G.; Vesce, L.; Caratto, V.; Mazzuca, C.; Gasiorowski, J.; Reale, A.; Di Carlo, A.; Brown, T.M. Formulations and processing of nanocrystalline TiO_2 films for the different requirements of plastic, metal and glass dye solar cell applications. *Nanotechnology* **2013**, *24*, 255401. [CrossRef]
24. Vesce, L.; Riccitelli, R.; Mincuzzi, G.; Orabona, A.; Soscia, G.; Brown, T.M.; Di Carlo, A.; Reale, A. Fabrication of spacer and catalytic layers in monolithic dye-sensitized solar cells. *IEEE J. Photovolt.* **2013**, *3*, 1004–1011. [CrossRef]
25. Mincuzzi, G.; Vesce, L.; Liberatore, M.; Reale, A.; Di Carlo, A.; Brown, T.M. Laser-sintered TiO_2 films for dye solar cell fabrication: An electrical, morphological, and electron lifetime investigation. *IEEE Trans. Electron Devices* **2011**, *58*, 3179–3188. [CrossRef]
26. Vesce, L.; Riccitelli, R. Processing and characterization of a TiO_2 paste based on small particle size powders for dye-sensitized solar cell semi-transparent photo-electrodes. *Prog. Photovolt. Res. Appl.* **2012**, *20*, 960–966. [CrossRef]
27. Ozawa, H.; Sugiura, T.; Kuroda, T.; Nozawa, K.; Arakawa, H. Highly efficient dye-sensitized solar cells based on a ruthenium sensitizer bearing a hexylthiophene modified terpyridine ligand. *J. Mater. Chem. A* **2016**, *4*, 1762–1770. [CrossRef]
28. Yella, A.; Mai, C.-L.; Zakeeruddin, S.-M.; Chang, S.-N.; Hsieh, C.-H.; Yeh, C.-Y.; Grätzel, M. Molecular Engineering of Push–Pull Porphyrin Dyes for Highly Efficient Dye-Sensitized Solar Cells: The Role of Benzene Spacers. *Angew. Chem. Int. Ed.* **2014**, *53*, 2973–2977. [CrossRef] [PubMed]
29. Eom, Y.K.; Kang, S.H.; Choi, I.T.; Yoo, Y.; Kim, J.; Kim, H.K. Significant light absorption enhancement by a single heterocyclic unit change in the π-bridge moiety from thieno[3,2-*b*]benzothiophene to thieno[3,2-*b*]indole for high performance dye-sensitized and tandem solar cells. *J. Mater. Chem. A* **2017**, *5*, 2297–2308. [CrossRef]

30. Zeng, K.; Chen, Y.; Zhu, W.-H.; Tian, H.; Xie, Y. Efficient Solar Cells Based on Concerted Companion Dyes Containing Two Complementary Components: An Alternative Approach for Cosensitization. *J. Am. Chem. Soc.* **2020**, *142*, 5154–5161. [CrossRef]
31. Dessì, A.; Calamante, M.; Sinicropi, A.; Parisi, M.L.; Vesce, L.; Mariani, P.; Taheri, B.; Ciocca, M.; Di Carlo, A.; Zani, L.; et al. Thiazolo[5,4-d]thiazole-based organic sensitizers with improved spectral properties for application in greenhouse-integrated dye-sensitized solar cells. *Sustain. Energy Fuels* **2020**, *4*, 2309–2321. [CrossRef]
32. Cao, Y.; Liu, Y.; Zakeeruddin, S.M.; Hagfeldt, A.; Grätzel, M. Direct Contact of Selective Charge Extraction Layers Enables High-Efficiency Molecular Photovoltaics. *Joule* **2018**, *2*, 1108–1117. [CrossRef]
33. Chen, C.-L.; Chang, T.-W.; Teng, H.; Wu, C.-G.; Chen, C.-Y.; Yang, Y.-M.; Lee, Y.-L. Highly efficient gel-state dye-sensitized solar cells prepared using poly(acrylonitrile-*co*-vinyl acetate) based polymer electrolytes. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3640–3645. [CrossRef] [PubMed]
34. Zhang, W.; Wu, Y.; Bahng, H.W.; Cao, Y.; Yi, C.; Saygili, Y.; Luo, J.; Liu, Y.; Kavan, L.; Moser, J.-E.; et al. Comprehensive control of voltage loss enables 11.7% efficient solid-state dye-sensitized solar cells. *Energy Environ. Sci.* **2018**, *11*, 1779–1787. [CrossRef]
35. Munoz-García, A.B.; Benesperi, I.; Boschloo, G.; Concepcion, J.J.; Delcamp, J.H.; Gibson, E.A.; Meyer, G.J.; Pavone, M.; Pettersson, H.; Hagfeldt, A.; et al. Dye-sensitized solar cells strike back. *Chem. Soc. Rev.* **2021**, *50*, 12450–12550. [CrossRef]
36. Vesce, L.; Guidobaldi, A.; Mariani, P.; Di Carlo, A.; Parisi, M.L.; Maranghi, S.; Basosi, R. World Scientific Reference of Hybrid Materials. World Scientific Publishing, Co., Pte Ltd.: Singapore, 2019; p. 423.
37. Vesce, L.; Mariani, P.; Calamante, M.; Dessì, A.; Mordini, A.; Zani, L.; Di Carlo, A. Process engineering of semitransparent DSSC modules and panel incorporating an organic sensitizer. *Solar RRL* **2022**, in press. [CrossRef]
38. Niu, G.; Guo, X.; Wang, L. Review of recent progress in chemical stability of perovskite solar cells. *J. Mater. Chem. A* **2015**, *3*, 8970–8980. [CrossRef]
39. Ansaria, M.I.H.; Qurashib, A.; Nazeeruddinc, M.K. Frontiers, opportunities, and challenges in perovskite solar cells: A critical review. *J. Photochem. Photobiol. C Photochem. Rev.* **2018**, *35*, 1–24. [CrossRef]
40. Asghar, M.I.; Zhang, J.; Wang, H.; Lund, P.D. Device stability of perovskite solar cells—A review. *Renew. Sustain. Energy Rev.* **2017**, *77*, 131–146. [CrossRef]
41. Kim, J.Y.; Lee, J.W.; Jung, H.S.; Shin, H.; Park, N.G. High-Efficiency Perovskite Solar Cells. *Chem. Rev.* **2020**, *120*, 7867–7918. [CrossRef] [PubMed]
42. Vesce, L.; Stefanelli, M.; Herterich, J.P.; Castriotta, L.A.; Kohlstädt, M.; Würfel, U.; Di Carlo, A. Ambient air blade-coating fabrication of stable triple-cation perovskite solar modules by green solvent quenching. *Solar RRL* **2021**, *5*, 2100073. [CrossRef]
43. Freitag, M.; Boschloo, G. The revival of dye-sensitized solar cells. *Curr. Opin. Electrochem.* **2017**, *2*, 111–119. [CrossRef]
44. Mariotti, N.; Bonomo, M.; Fagiolari, L.; Barbero, N.; Gerbaldi, C.; Bella, F.; Barolo, C. Recent advances in eco-friendly and cost-effective materials towards sustainable dye-sensitized solar cells. *Green Chem.* **2020**, *22*, 7168–7218. [CrossRef]
45. Parisi, M.L.; Dessì, A.; Zani, L.; Maranghi, S.; Mohammadpourasl, S.; Calamante, M.; Mordini, A.; Basosi, R.; Reginato, G.; Sinicropi, A. Combined LCA and Green Metrics Approach for the Sustainability Assessment of an Organic Dye Synthesis on Lab Scale. *Front. Chem.* **2020**, *8*, 214. [CrossRef] [PubMed]
46. Bella, F.; Galliano, S.; Falco, M.; Viscardi, G.; Barolo, C.; Grätzel, M.; Gerbaldi, C. Approaching truly sustainable solar cells by the use of water and cellulose derivatives. *Green Chem.* **2017**, *19*, 1043–1051. [CrossRef]
47. Lee, C.P.; Li, C.T.; Ho, K.C. Use of organic materials in dye-sensitized solar cells. *Mater. Today* **2017**, *20*, 267–283. [CrossRef]
48. Bella, F.; Gerbaldi, C. Natural Polymers for Dye-Sensitized Solar Cells: Electrolytes and Electrodes. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons: Hoboken, NJ, USA, 2016.
49. Schoden, F.; Dotter, M.; Knefelkamp, D.; Blachowicz, T.; Schwenzfeier Hellkamp, E. Review of State of the Art Recycling Methods in the Context of Dye Sensitized Solar Cells. *Energies* **2021**, *14*, 3741. [CrossRef]
50. Pandey, S.; Karakoti, M.; Surana, K.; Dhapola, P.S.; Bhushan, B.S.; Ganguly, S.; Singh, P.K.; Abbas, A.; Srivastava, A.; Sahoo, N.G. Graphene nanosheets derived from plastic waste for the application of DSSCs and supercapacitors. *Sci. Rep.* **2021**, *11*, 3916. [CrossRef] [PubMed]
51. Soudi, N.; Nanayakkara, S.; Jahed, N.M.S.; Naahidi, S. Rise of nature-inspired solar photovoltaic energy convertors. *Sol. Energy* **2020**, *208*, 31–45. [CrossRef]
52. Page, C.C.; Moser, C.C.; Chen, X.; Dutton, P.L. Natural Engineering Principles of Electron Tunneling in Biological Oxidation-Reduction. *Nature* **1999**, *402*, 47–52. [CrossRef] [PubMed]
53. Wasielewski, M.R. Photoinduced electron transfer in supramolecular systems for artificial photosynthesis. *Chem. Rev.* **1992**, *92*, 435–461. [CrossRef]
54. Beratan, D.N.; Onuchic, J.N.; Winkler, J.R.; Gray, H.B. Electron-tunneling pathways in proteins. *Science* **1992**, *258*, 1740–1741. [CrossRef]
55. Sek, S.; Misicka, A.; Swiatek, K.; Maicka, E. Asymmetry of electron transmission through monolayers of helical polyalanine adsorbed on gold surfaces. *J. Phys. Chem. B* **2005**, *109*, 18433–18438. [CrossRef] [PubMed]
56. Galoppini, E.; Fox, M.A. Effect of the electric field generated by the helix dipole on photoinduced intramolecular Electron Transfer in dichromophoric α-helical peptides. *J. Am. Chem. Soc.* **1996**, *118*, 2299–2300. [CrossRef]
57. Fox, M.A.; Galoppini, E. Electric field effect on Electron Transfer rates in dichromophoric peptides: The effect of helix unfolding. *J. Am. Chem. Soc.* **1997**, *119*, 5277–5285. [CrossRef]

58. Watanabe, J.; Morita, T.; Kimura, S. Effects of dipole moment, linkers and chromophores at side chains on long-range Electron Transfer through helical peptides. *J. Phys. Chem. B* **2005**, *109*, 14416–14425. [CrossRef] [PubMed]
59. Gatto, E.; Porchetta, A.; Stella, L.; Guryanov, I.; Formaggio, F.; Toniolo, C.; Kaptein, B.; Broxterman, Q.B.; Venanzi, M. Conformational Effects on the Electron-Transfer Efficiency in Peptide Foldamers Based on α,α-Disubstituted Glycyl Residues. *Chem. Biodivers.* **2008**, *5*, 1263–1278. [CrossRef]
60. Gatto, E.; Stella, L.; Baldini, C.; Venanzi, M.; Toniolo, C.; Formaggio, F. Photocurrent generation in peptide-based self-assembled monolayers on gold electrodes. *Superlatt. Microstruct.* **2009**, *46*, 34–39. [CrossRef]
61. Gatto, E.; Porchetta, A.; Scarselli, M.; De Crescenzi, M.; Formaggio, F.; Toniolo, C.; Venanzi, M. Playing with Peptides: How to Build a Supramolecular Peptide Nanostructure by Exploiting Helix···Helix Macrodipole Interaction. *Langmuir* **2012**, *28*, 2817–2826. [CrossRef] [PubMed]
62. Venanzi, M.; Gatto, E.; Caruso, M.; Porchetta, A.; Formaggio, F.; Toniolo, C. Photoinduced Electron Transfer through Peptide-Based Self-Assembled Monolayers Chemisorbed on Gold Electrodes: Directing the Flow-in and Flow-out of Electrons through Peptide Helices. *J. Phys. Chem. A* **2014**, *118*, 6674–6684. [CrossRef]
63. Shin, Y.K.; Newton, M.D.; Isied, S.S. Distance dependence of Electron Transfer across peptides with different secondary structures: The role of peptide energetic and electronic coupling. *J. Am. Chem. Soc.* **2003**, *125*, 3722–3732. [CrossRef] [PubMed]
64. Creager, S.; Yu, C.J.; Bamdad, C.; O'Connor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G.T.; Luo, J.; Gozin, M.; et al. Electron Transfer at Electrodes through Conjugated "Molecular Wire" Bridges. *J. Am. Chem. Soc.* **1999**, *121*, 1059–1064. [CrossRef]
65. Fan, F.-R.F.; Yao, Y.; Cai, L.; Cheng, L.; Tour, J.M.; Bard, A.J. Structure-Dependent Charge Transport and Storage in Self-Assembled Monolayers of Compounds of Interest in Molecular Electronics: Effects of Tip Material, Headgroup, and Surface Concentration. *J. Am. Chem. Soc.* **2004**, *126*, 4035–4042. [CrossRef] [PubMed]
66. Davis, W.B.; Svec, W.A.; Ratner, M.A.; Wasielewski, M.R. Molecular-wire behaviour in *p*-phenylenevinylene oligomers. *Nature* **1998**, *396*, 60–63. [CrossRef]
67. Sikes, H.D.; Smalley, J.F.; Dudek, S.P.; Cook, A.R.; Newton, M.D. Rapid electron tunneling through oligophenylenevinylene bridges. *Science* **2001**, *291*, 1519–1523. [CrossRef] [PubMed]
68. Rao, K.K.; Hall, D.O.; Vlachopoulos, N.; Grätzel, M.; Evans, M.C.V.; Seibert, M. Photoelectrochemical responses of photosystem II particles immobilized on dye-derivatized TiO_2 films. *J. Photochem. Photobiol. B* **1990**, *5*, 379–389. [CrossRef]
69. Ciesielski, P.N.; Scott, A.M.; Faulkner, C.J.; Berron, B.J.; Cliffel, D.E.; Jennings, G.K. Functionalized Nanoporous Gold Leaf Electrode Films for the Immobilization of Photosystem I. *ACS Nano* **2008**, *2*, 2465–2472. [CrossRef] [PubMed]
70. Yehezkeli, O.; Tel-Vered, R.; Wasserman, J.; Trifonov, A.; Michaeli, D.; Nechushtai, R.; Willner, I. Integrated photosystem II-based photo-bioelectrochemical cells. *Nat. Commun.* **2012**, *3*, 742–745. [CrossRef] [PubMed]
71. Onoda, A.; Kakikura, Y.; Uematsu, T.; Kuwabata, S.; Hayashi, T. Photocurrent Generation of Hierarchical Zinc-substituted Hemoprotein Assemblies Immobilized on a Gold Electrode. *Angew. Chem. Int. Ed.* **2012**, *51*, 2628–2631. [CrossRef] [PubMed]
72. Mershin, A.; Matsumoto, K.; Kaiser, L.; Yu, D.; Vaughn, M.; Nazeeruddin, M.K.; Bruce, B.D.; Graetzel, M.; Zhang, S. Self-assembled photosystem-I biophotovoltaics on nanostructured TiO_2 and ZnO. *Sci. Rep.* **2012**, *2*, 234. [CrossRef] [PubMed]
73. Fang, X.; Kalathil, S.; Reisner, E. Semi-biological approaches to solar-to-chemical conversion. *Chem. Soc. Rev.* **2020**, *49*, 4926–4952. [CrossRef] [PubMed]
74. Thavasi, V.; Lazarova, T.; Filipek, S.; Kolinski, M.; Querol, E.; Kumar, A.; Ramakrishna, S.; Padrós, E.; Renugopalakrishnan, V. Study on the Feasibility of Bacteriorhodopsin as Bio-Photosensitizer in Excitonic Solar Cell: A First Report. *J. Nanosci. Nanotechnol.* **2008**, *8*, 1679–1687. [CrossRef]
75. Yasutomi, S.; Morita, T.; Imanishi, Y.; Kimura, S. A molecular photodiode system that can switch photocurrent direction. *Science* **2004**, *304*, 1944–1947. [CrossRef] [PubMed]
76. Yanagisawa, K.; Morita, T.; Kimura, S. Efficient photocurrent generation by self-assembled monolayers composed of 3_{10}-helical peptides carrying linearly spaced Naphthyl groups at the side chains. *J. Am. Chem. Soc.* **2004**, *126*, 12780–12781. [CrossRef]
77. Morita, T.; Kimura, S.; Kobayashi, S.; Imanishi, Y. Photocurrent generation under a large dipole moment formed by self-assembled monolayers of helical peptides having an *N*-Ethylcarbazolyl group. *J. Am. Chem. Soc.* **2000**, *122*, 2850–2859. [CrossRef]
78. Yasutomi, S.; Morita, T.; Kimura, S. pH-controlled switching of photocurrent detection by self-assembled monolayer of helical peptides. *J. Am. Chem. Soc.* **2005**, *127*, 14564–14565. [CrossRef] [PubMed]
79. Gatto, E.; Venanzi, M.; Palleschi, A.; Stella, L.; Pispisa, B.; Lorenzelli, L.; Toniolo, C.; Formaggio, F.; Marletta, G. Self-assembled peptide monolayers on interdigitated gold microelectrodes. *Mater. Sci. Eng. C* **2007**, *27*, 1309–1312. [CrossRef]
80. Gatto, E.; Stella, L.; Formaggio, F.; Toniolo, C.; Lorenzelli, L.; Venanzi, M. Electroconductive and photocurrent generation properties of self-assembled monolayers formed by functionalized, conformationally constrained peptides on gold electrodes. *J. Pept. Sci.* **2008**, *14*, 184–191. [CrossRef] [PubMed]
81. Gatto, E.; Caruso, M.; Porchetta, A.; Toniolo, C.; Formaggio, F.; Crisma, M.; Venanzi, M. Photocurrent generation through peptide-based self-assembled monolayers on a gold surface: Antenna and junction effects. *J. Pept. Sci.* **2011**, *17*, 124–131. [CrossRef] [PubMed]
82. Gatto, E.; Venanzi, M. Self-assembled monolayers formed by helical peptide building blocks: A new tool for bioinspired nanotechnology. *Polym. J.* **2013**, *45*, 468–480. [CrossRef]
83. Gatto, E.; Venanzi, M. Peptronics: Peptide Materials for Electron Transfer. In *Peptide Materials from Nanostructures to Applications*; Alemàn, C., Bianco, A., Venanzi, M., Eds.; Wiley-VCH: Weinheim, Germany, 2013; pp. 105–147.

84. Gatto, E.; Venanzi, M. The Impervious Route to Peptide-Based Dye-Sensitized Solar Cells. *Isr. J. Chem.* **2015**, *55*, 671–681. [CrossRef]
85. Gatto, E.; Kubitzky, S.; Schriever, M.; Cesaroni, S.; Mazzuca, C.; Venanzi, M.; De Zotti, M. Building Supramolecular DNA-Inspired Nanowires on Gold Surface: From 2D to 3D. *Angew. Chem.* **2019**, *58*, 7308–7312. [CrossRef]
86. Kubitzky, S.; Venanzi, M.; Biondi, B.; Lettieri, R.; De Zotti, M.; Gatto, E. A pH-Induced Reversible Conformational Switch Able to Control the Photocurrent Efficiency in a Peptide Supramolecular System. *Chem. Eur. J.* **2021**, *27*, 2810–2817. [CrossRef] [PubMed]
87. Umehara, S.; Pourmand, N.; Webb, C.D.; Davis, R.W.; Yasuda, K.; Karhanek, M. Current rectification with poly-L-lysine-coated quartz nanopipettes. *Nano Lett.* **2006**, *6*, 2486–2492. [CrossRef] [PubMed]
88. Gatto, E.; Quatela, A.; Caruso, M.; Tagliaferro, R.; De Zotti, M.; Formaggio, F.; Toniolo, C.; Di Carlo, A.; Venanzi, M. Mimicking Nature: A Novel Peptide-based Bio-inspired Approach for Solar Energy Conversion. *ChemPhysChem* **2014**, *15*, 64–68. [CrossRef] [PubMed]
89. Caruso, M.; Gatto, E.; Palleschi, A.; Morales, P.; Scarselli, M.; Casaluci, S.; Quatela, A.; Di Carlo, A.; Venanzi, M. A bioinspired dye sensitized solar cell based on a rhodamine-functionalized peptide immobilized on nanocrystalline TiO_2. *J. Photochem. Photobiol. A Chem.* **2017**, *347*, 227–234. [CrossRef]
90. Karthikeyan, C.; Thelakkat, M.; Willert-Porada, M. Different mesoporous titania films for solid-state dye sensitised solar cells. *Thin Solid Film.* **2006**, *511*, 187–194. [CrossRef]
91. Kim, Y.J.; Lee, M.H.; Kim, H.J.; Lim, G.; Choi, Y.S.; Park, N.-G.; Kim, K.; Lee, W.I. Formation of Highly Efficient Dye-Sensitized Solar Cells by Hierarchical Pore Generation with Nanoporous TiO_2 Spheres. *Adv. Mater.* **2009**, *21*, 3668–3673. [CrossRef]
92. Schlichthörl, G.; Huang, S.; Sprague, J.; Frank, A. Band Edge Movement and Recombination Kinetics in Dye-Sensitized Nanocrystalline TiO_2 Solar Cells: A Study by Intensity Modulated Photovoltage Spectroscopy. *J. Phys. Chem. B* **1997**, *101*, 8141–8155. [CrossRef]
93. Grätzel, M. Recent Advances in Sensitized Mesoscopic Solar Cells. *Acc. Chem. Res.* **2009**, *42*, 1788–1798. [CrossRef] [PubMed]
94. Han, T.H.; Moon, H.S.; Hwang, J.O.; Seok, S.I.; Im, S.H.; Kim, S.O. Peptide-templating dye-sensitized solar cells. *Nanotechnology* **2010**, *21*, 185601. [CrossRef]
95. Acar, H.; Garifullin, R.; Aygun, L.E.; Okyayab, A.K.; Guler, M.O. Amyloid-like peptide nanofiber templated titania nanostructures as dye sensitized solar cell anodic materials. *J. Mater. Chem. A* **2013**, *1*, 10979–10984. [CrossRef]
96. Reches, M.; Gazit, E. Casting metal nanowires within discrete self-assembled peptide nanotubes. *Science* **2003**, *300*, 625–627. [CrossRef] [PubMed]