Review Article

Improving the stability of photosystem I−based bioelectrodes for solar energy conversion

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Abstract

Isolated photosystem I (PSI) has been integrated into numerous technologies for solar energy conversion. Interest in PSI is a consequence of its high internal quantum efficiency, thermal stability, ease of extraction, and adaptability. While there has been success in improving performance to elevate PSI biohybrid technologies toward a practical realm, the stability of PSI bioelectrodes is also of critical importance. Commercial solar energy conversion technologies are expected to achieve lifetimes of the order of ten years; however, many research-scale PSI bioelectrodes have only been tested for tens of days. Key areas affecting PSI bioelectrode stability include the effects of reactive oxygen species, immobilization strategies, and the environment within solid-state PSI biohybrid photovoltaics. At the current state, further investigation of long-term stability is necessary in enabling the development of PSI bioelectrodes for both photoelectrochemical cells and solid-state biohybrid photovoltaics.

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Introduction

Photoactive protein complexes that drive photosynthesis are internally efficient, with more than 99% of captured photons resulting in electron−hole pairs, or excitons, used for the production of chemical energy [1,2]. Photosystem I (PSI) is one of the two primary protein complexes found within the thylakoid membrane of plants, algae, and cyanobacteria [1−3]. PSI is a plastocyanin−ferredoxin oxidoreductase that captures photonic energy via delocalization of electrons within a network of chlorophyll antennae [2]. Electron transfer within PSI begins with the excitation of the P_{700} reaction center, followed by transport of the electron to an iron−sulfur cluster, F_B, where ferredoxin reduction occurs [2]. PSI has been targeted as a low-cost and benign photosensitizer, primarily owing to its high reduction potential and exceptional thermal stability [1−6]. Interest in PSI has also been attributed to its ease of extraction, compatibility with inorganic materials, reactivity with common electrochemical mediators, and capacity for genetic engineering [4,7−9]. Thanks to these desirable properties, isolated PSI has been implemented in a variety of energy conversion technologies including photoelectrochemical cells, biohybrid photovoltaics, and dye-sensitized solar cells [4,7,9−12]. Research on PSI has been focused on its integration with electrode materials, electrochemical mediators, and electron and hole transport layers [4,7−9,13,14]. Several recent investigations have also explored its incorporation into solid-state devices to improve performance and practicality in the field of solar energy conversion [4,7,9,15].

The long-term stability of PSI within bioelectrodes is becoming increasingly important, especially in technologies such as biohybrid photovoltaics [7,9,16]. Long-term stability is critical when incorporating biological materials into energy conversion systems that are expected to have lifetimes of the order of ten years [17]. The stability of the PSI protein complex is largely related to its immediate environment; the natural
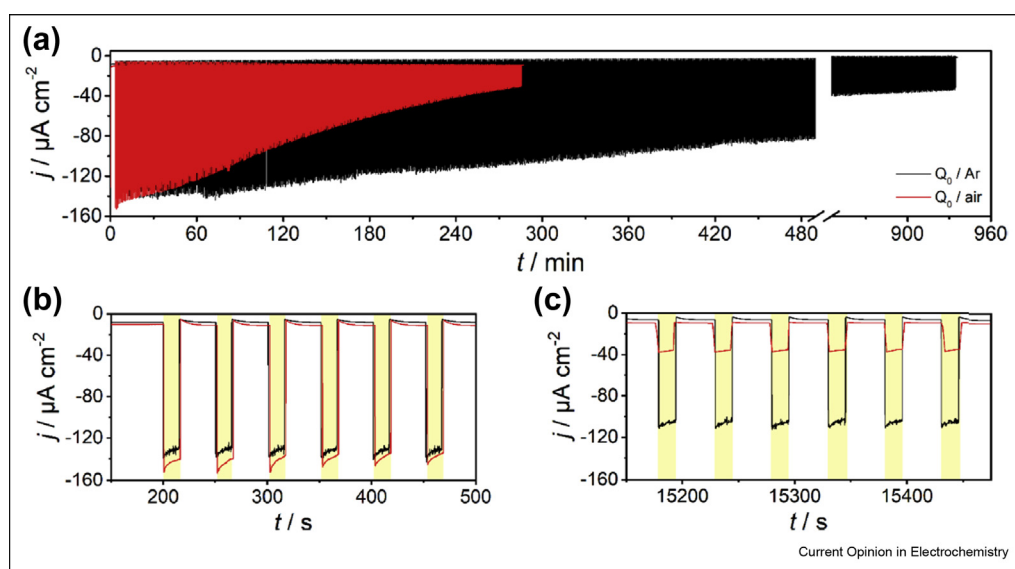
environment of PSI is dynamic, and PSI is responsive to stresses including changes in temperature, fluctuations in metabolite concentrations, and protein complex conformation within chloroplasts [16]. One avenue for retaining stability of photosynthetic protein complexes is to incorporate the entire thylakoid membrane into biohybrid devices. Recent advances in this field include the addition of osmolytes to improve thermal stability and the immobilization of thylakoid membranes onto graphene scaffolds, which increases the likelihood of the desired electron transfer pathway and minimizes damaging internal processes [18,19]. However, when designing biohybrid systems using isolated PSI, the extraction procedure, solvent and surfactant properties, and the environment surrounding the protein complex are critical in determining the stability — both structural and performance-related stability — within bioelectrodes [9,16]. Herein, we discuss and evaluate the current state of PSI bioelectrodes with respect to the overall stability of the protein complex outside of its native environment. We highlight three areas regarding PSI stability: the effects of aerobic electrolytes, including damage by reactive oxygen species (ROS), immobilization strategies for improvement of photocurrent production and physical bioelectrode stability, and the incorporation of PSI into solid-state biohybrid photovoltaics. We conclude that although solid-state devices require protein immobilization and may mitigate known stability issues such as ROS damage, gaps

remain in the understanding of PSI stability in these systems, and there is a great need for further research.

Aerobic electrolytes and degradation by ROS

Owing to both practicality and knowledge from previous research efforts, aerobic electrolytes are commonly used to produce high-performing bioelectrodes [7]. Despite the advantages of dissolved oxygen as a mediator, it is reported to be problematic, allowing for the production of ROS and the consequential degradation of the PSI structure and function [20,21*]]. The production of ROS by PSI within chloroplasts of plants is well known [22]. ROS is known to stimulate photoinhibition *in vivo* by damaging the active sites of photosynthetic protein complexes [20]. Superoxide (O_2^-) and singlet oxygen ($^1O_2$) may be produced by PSI and are detoxified by superoxide dismutase and ascorbate peroxidase enzymes [20]. The absence of essential protective enzymes in PSI bioelectrodes means that the presence of ROS is detrimental and has been reported to cause damage to the P_{700} site [20]. Zhao et al. [21*] reported that PSI deposited within the biocathode containing a mixture of an osmium redox polymer and poly(ethylene glycol) diglycidyl ether produces ROSs that are detectable through the collection of hydrogen peroxide via scanning photoelectrochemical microscopy. Zhao et al. [21*] also found that the production of ROS occurs even in the presence of other artificial mediators, and
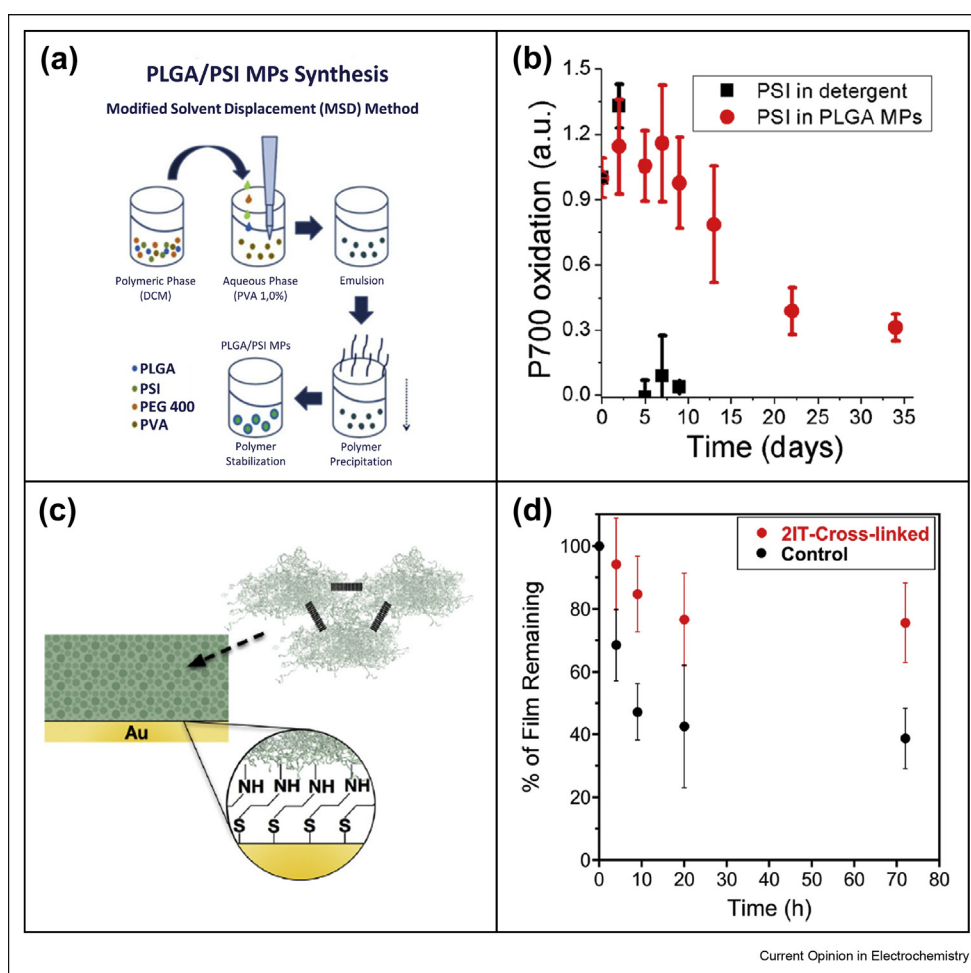
Figure 1

Stability study of PSI−Os$_p$−PEGDGE biocathodes. **(a)** A comparison of photocurrent density stability in air-equilibrated (red) and anaerobic argon (black) conditions. **(b)** Expanded views of the data from panel a are given for the initial few minutes of the study. **(c)** Expanded views of the data from panel a are given after 4 h of the study. Yellow sections denote illumination by a light source of 80 mW/cm^2 in the presence of a phosphate−citrate buffer (pH = 4.0) electrlolyte containing 2.5 mM Q$_0$. The applied potential of the cell was 300 mV vs. SHE (reproduced with permission from Zhao et al [24**], Copyright 2019 American Chemical Society). PSI, photosystem I; PEGDGE, poly(ethylene glycol) diglycidyl ether; SHE, standard hydrogen electrode.

they claim that the suppression of ROS production within PSI bioelectrodes will be difficult owing to the high reactivity and short diffusion time of ROS [21].

Other studies have proven that the presence of oxygen is vital to the performance of PSI bioelectrodes using specific mediators, further complicating stability issues related to ROS [23,24**]]. Zhao et al. [24**] showed that within the osmium redox polymer—poly(ethylene glycol) diglycidyl ether biocathode, the presence of oxygen is necessary for electron transfer when using methyl viologen as an electron acceptor, making a performance stability study using this mediator impossible

in deaerated conditions. To circumvent the problem, ubiquinone (Q_0) was used as a replacement electron acceptor owing to its similar performance in the presence and absence of oxygen. As shown in Figure 1, the degradation of a PSI biocathode in the presence of Q_0 was found to be linear and slower in the absence of oxygen, retaining 77% of its photocurrent performance after 4 h. In the presence of oxygen, the degradation rate increased dramatically, after a first-order decay with a k_{app} of 1.05×10^{-4} s^{-1} and retaining only 32% of the original photocurrent after 4 h [24**]. Ciornii et al. [25*] showed that adding the electron-scavenging Q_0 to porous indium tin oxide—cytochrome complex (cyt c)—

Figure 2

Examples of PSI immobilization strategies designed to improve PSI bioelectrode stability. **(a)** The modified solvent displacement method as used to produce poly lactic-co-glycolic acid (PLGA)-PSI microparticles (MPs) (reproduced and adapted with permission from Cherubin et al [47**], Copyright 2019 American Chemical Society, further permissions regarding this material should be directed to the ACS, https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.9b00738). **(b)** P$_{700}$ oxidation as a function of time demonstrates that PSI entrapped within PLGA MPs resists photobleaching over time (reproduced with permission from Cherubin et al [47**], Copyright 2019 American Chemical Society, further permissions regarding this material should be directed to the ACS, https://pubs.acs.org/doi/abs/10.1021/acssuschemeng.9b00738). **(c)** A schematic of a cross-linked PSI multilayer produced by introducing 2IT into a PSI multilayer deposited onto an amine-terminated self-assembled monolayer (SAM) (reproduced with permission from Yang et al [48], Copyright 2016 Elsevier). **(d)** A PSI multilayer film and cross-linked multilayer film retention study performed in aqueous electrolyte showing 75 h of stability (reproduced with permission from Yang et al [48], Copyright 2016 Elsevier). PSI, photosystem I; 2IT, 2-iminothiolane; DCM, dichloromethane; PVA, polyvinyl alcohol.

PSI electrodes lowers the rate of photocurrent degradation in a 30-min short-pulse (20-s) light stability study. In addition to anaerobic aqueous electrolytes and the addition of electron scavengers, a cobalt[II/III]-based mediator in an organic solvent and a designer surfactant peptide, A_6K, was used by Mershin et al. [26] to improve the structure—function stability of PSI [27]. These findings, along with the previously mentioned issues related to ROS, should be considered as a testament to the need for novel anaerobic electrolytes and other methods for mitigating ROS production as a direction for improving PSI bioelectrode stability.

Immobilization: covalent attachment and entrapment strategies

The immobilization of PSI onto various electrode surfaces has been a common direction for increasing photoactivity and stability of PSI bioelectrodes [4,7,9,28,29]. In general, there have been two directions for improvement via PSI immobilization. The first is to immobilize PSI through either covalent linkage or physical attraction to an electrode or another active component to enhance electron transfer [30—35]. Despite improved performance, there are few findings supporting stability beyond a single day in these PSI bioelectrodes. However, efforts aimed toward achieving direct electron transfer should be noted because they indirectly provide physical stability through immobilization. A number of recent studies have investigated the use of cyt c as an electron shuttle for PSI in biocathodes [14,25,33,36—38]. The mechanism of binding and electron transfer to PSI via cyt c has been extensively studied for the purpose of improving the electron transfer between the cathode and P_{700} [39—42]. Alternative linking agents have also been investigated, including a perylene diimide derivative, which transfers charge from PSI to platinum nanoparticles for hydrogen evolution, and lumogen red as an artificial antenna for electron transfer on a titanium dioxide electrode [30,34]. PSI has been linked or immobilized via chemical and physical methods onto other materials, including alkanethiol self-assembled monolayers on gold, graphene, glassy carbon via an osmium polymer, and fullerene C70 [29,43—45]. Finally, other strategies such as phage display, plasmon coupling, and linking to dehydrogenase have been developed for improving electron transfer in PSI bioelectrodes [31,35]. Each of these linking strategies has improved electron transfer from PSI to a substrate electrode. Although stability is not the primary focus, efforts toward achieving improved electron transfer may indirectly improve the PSI—electrode interface by physically or chemically binding the protein to a surface.

PSI immobilization has also been targeted as a direct strategy for improving the physical stability of the PSI—electrode interface. Examples include covalent linkage of PSI complexes within a thick multilayer film and entrapment of the protein complex within gels, microspheres, or porous electrodes [23,33,46,47**,48]. These strategies improve physical stability by minimizing desorption and dissolution of the multilayer films into the electrolyte. Entrapment also brings the protein into a new environment, protecting it from hazardous species in solution or from flow in the bulk electrolyte. To improve stability, Cherubin et al. [47**] encapsulated PSI into chitosan and polylactic-co-glycolic acid—based microparticles (MPs) using a modified solvent displacement method (Figure 2 (a)). The polylactic-co-glycolic acid—PSI MPs increased resistance to photobleaching from 5 to more than 34 days, as shown in Figure 2 (b) [47**]. Resistance to photobleaching was attributed to protection of the protein within the amphiphilic MPs. Badura et al. [23] showed that covalent linkage to an osmium-based redox polymer protects the protein complex. Specifically, the redox polymer shields PSI from direct contact with the bulk electrolyte. In addition, Zhao et al. showed that interactions within a similar osmium-based hydrogel may be tuned via the pH-dependent moieties within the polymer [49]. In a general effort to improve PSI multilayer stability, Yang et al. [48] cross-linked multilayers of PSI to minimize desorption into solution over time. Cross-linking of PSI via disulfide bonds using 2-iminothiolane, as depicted in Figure 2 (c), increased the percentage of PSI complexes retained on the bioelectrode over a 3-day exposure to the electrolyte (Figure 2 (d)) [48]. In summary, the overall stability of PSI bioelectrodes within liquid electrochemical cells can be improved through covalent linkage and cross-linking, physical interactions, and encapsulation, which effectively mitigate desorption, dissolution, and interaction with the bulk electrolyte.

Solid-state biohybrid photovoltaics

PSI photovoltaics composed of all solid components have advantages in regard to practicality, performance, and stability [7,9]. By eliminating the liquid electrolyte, the PSI protein complex is protected from soluble species, such as ROS, and is immobilized between electrodes. In addition, liquid electrolytes add unnecessary weight to the cell, may evaporate in hot environments, and can leak, causing corrosion of metal components over time. Many aspects of solid-state biohybrid systems are not well understood, especially regarding the stability of the photoactive biological species within these novel environments. The standard analysis of a solid-state PSI biohybrid photovoltaic begins with a layered device schematic and a band energy diagram showing the electron energy within each distinct layer and the path of electron flow. Solid-state PSI biohybrid photovoltaics comprise two current collectors (one being transparent), electron and hole transport layers, and a PSI-based photoactive layer.
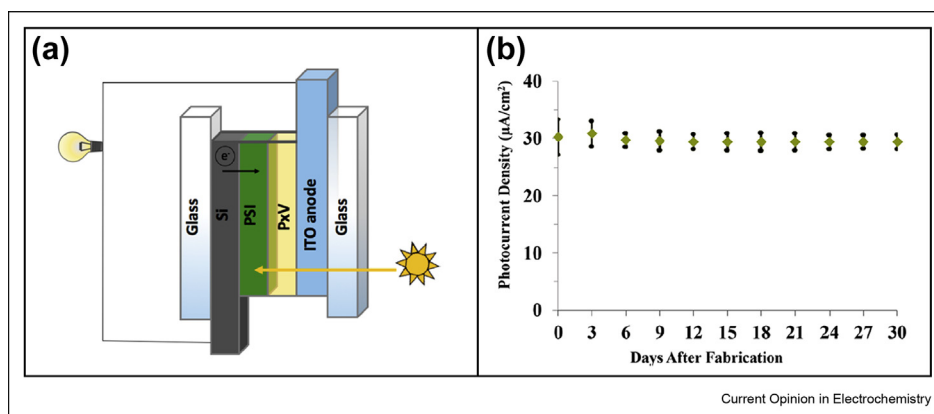
Materials are chosen based on their energetics, with the final photopotential of the cell determined by the electron energy at the two current collectors and the total resistance of all layers.

Solid-state devices differ from photoelectrochemical cells with a liquid electrolyte in both the chosen materials and in deposition techniques. The deposition technique is an important consideration in preparing the PSI active layer. Common deposition strategies include low-vacuum deposition, spin coating, and entrapment within conducting polymer matrices [50,51*,52,53*,54–57]. These techniques are chosen because their benign conditions are unlikely to cause damage to or denature PSI. Furthermore, the hydration of the protein complex within the film is critical to its performance and structural stability, favoring solution-phase deposition techniques [51*,58]. Designer peptide detergents have been used by Kiley et al. [58] to improve structural stability during the deposition of solid-state PSI films and by Matsumoto et al. [59] for long-term structural stability in aqueous solvents. Within biohybrid photovoltaic devices, PSI active layers must be deposited in a manner that allows for moisture retention, and subsequent layers must be deposited with caution [51*,53*,54]. While the need for hydration of the protein complex within solid devices is established, little has been reported on structure–function properties or stability for various states of hydration or within different environments.

Performance within solid-state PSI biohybrid photovoltaics has improved drastically in the past five years. Improvements are attributed to novel material choices and deposition strategies, including those aimed toward imp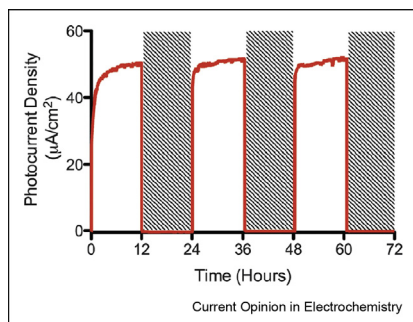roved PSI orientation. Performance of solid-state devices is most often represented using a power curve, from which the fill factor and power conversion efficiency (PCE) can be ascertained. Gordiichuk et al. [50] produced a solid-state PSI device that incorporates a titanium oxide anode, a semiconducting polytriaryl-amine polymer hole transport layer, and a molybdenum oxide cathode, achieving a fill factor of 45%. Zeynali et al. [51*] produced a solid-state device yielding one of the highest reported PCEs of a PSI solid-state photovoltaic, achieving 0.51% by incorporating high-performing hole and electron transport layers. Other recently reported all-solid-state PSI biohybrid photovoltaics include a solid-state device based on a PSI multilayer interfaced with poly(3,4-ethylenedioxythiophene):polystyrene sulfonate prepared by Kazemzadeh et al. [54], a PSI-cyt c composite device prepared by Olmos et al.[56], and a PSI-polyaniline solid-state device prepared by Gizzie et al. [55]. Although solid-state devices are generally assumed to offer improved stability, thanks to their mitigation of both dissolution or desorption and the absence of hazardous soluble species, little experimental evidence has been demonstrated. Figure 3(a) shows a schematic of a high-performing solid-state PSI biohybrid photovoltaic prepared by Dervishogullari et al. [53*], which was tested for photocurrent performance stability for 30 days (Figure 3(b)). Beam et al. [57] also highlighted the stability of a p-type silicon/PSI/zinc oxide device for 20 days. In another multiday stability study, a polyaniline–PSI composite device yielded a photocurrent of more than 60 μA/cm² after 3 days of continuous testing under 12-h light cycles, showing this device may be used on a practically relevant daily timescale (Figure 4) [55]. Although these studies are promising, further improvement of performance along with a heavier emphasis on long-term stability is necessary for PSI biohybrid solid-

Figure 3

Dervishogullari et al. [53*] fabricated a solid-state PSI biohybrid photovoltaic incorporating a polyviologen electron transport layer. **(a)** A device schematic highlighting the transparent indium tin oxide (ITO) anode and polyviologen electron transport layer (reproduced with permission from Dervishogullari et al [53*], Copyright 2018 American Chemical Society). **(b)** A 30-day performance stability study showing the photocurrent produced as a function of days passed since the device fabrication scale (reproduced with permission from Dervishogullari et al [53*], Copyright 2018 American Chemical Society). PSI, photosystem I.

Figure 4

A 12-h light cycle stability study highlighting the stability of the PSI–polyaniline solid-state device produced by Gizzie et al. [55] on a practically relevant timescale (reproduced with permission from Gizzie et al [55], Copyright 2015 Royal Society of Chemistry). PSI, photosystem I.

state photovoltaics to be used in practical applications, especially in regard to the presence of oxygen within solid-state devices.

Conclusions

The rapid development of PSI bioelectrodes warrants consideration of the stability of the protein complex in a variety of environments. Aerobic electrolytes are both practical and have high performance; however, the production of damaging ROS may limit the possibility of long-term stability [24**]. Means of protecting the protein complex from ROS are therefore necessary for the use of mediators that require an aerobic environment, such as methyl viologen. Immobilization strategies have been developed to retain the PSI protein complex in a structurally stable environment and to protect it from the electrolyte. Both entrapment and cross-linking have been used to improve the stability of PSI [47**,48]. A push toward solid-state PSI biohybrid photovoltaics may offer a solution to both ROS degradation and protein immobilization, while also eliminating other limitations associated with liquid electrolytes. Many promising materials and deposition strategies have been developed, and PCEs near the single-digit range have been reported [51*]. However, the longest reported duration of a performance stability study for a solid-state device is only 30 days [53*]. Researchers should begin to consider factors such as hydration, the presence of oxygen, photobleaching, and the structure of PSI in these novel solid-state environments in an effort to improve long-term stability. Solid-state devices show promise for the future of PSI-based technologies, and their stability will become increasingly important in the development of PSI biohybrid photovoltaics

Conflict of interest

None declared.

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Papers of particular interest, published within the period of review, have been highlighted as:

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