



Review—Combining Experimental and Engineering Aspects of Catalyst Design for Photoelectrochemical Water Splitting

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Hydrogen is one of the cleanest, most favourable, and most practical energy transferors. However, its efficient generation, storage and transportation are still a challenge. There are various routes available toward greener hydrogen. Solar-driven splitting is considered a cleaner method with no harmful emission and viability of up-scaling. Various semiconductors were studied for photo-electrochemical catalysis to improve overall efficiency of the system (i.e. Solar-to-Hydrogen (STH)). The insistence of framing this article is to offer an intense evaluation of scientific and technical aspects of available designing strategies' for photocatalysts and recent fruitful advancements towards product development. This review might act as a handbook for budding researchers and provide a cutting-edge towards innovative & efficient catalyst designing strategy to improve efficiency for working scientists.

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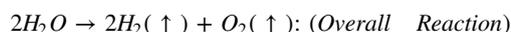
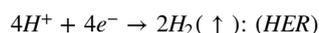
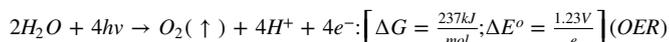


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To address escalating energy demands every year, which will touch the figure of ~38700 TW/hr by 2050, and research is going on to make a smooth swift from fossil reserves to renewable resources, the research community¹ makes constant efforts. However, realizing an economy based on renewable energies still requires more tedious efforts as the more significant fraction of energy obtained by renewable resources uses fossil fuels as their feedstock.² As these fossil fuels are a rich source of carbon and can be used to produce various precious chemical productions, they are of limited availability.³ Hence, it is our prior responsibility to protect them before they are completely exhausted. When we knock on the doors for renewable energy, Mother Nature has blessed us with abundant resources of sunlight (>99.9%) and water (~71% on the whole earth).⁴ Combining these two fascinating magical ingredients makes it possible to break water molecules to create one of the promising future renewable fuels, i.e., hydrogen. This process is known as water splitting & can be carried out by several means, including photocatalysis, electrocatalysis, photo-electrochemical, thermochemical, and photovoltaic assisted electrochemical routes.^{5,6} Apart from this approach, various techniques are already based on heating energy resources, as listed in Fig. 1. All these techniques (individually) are research domains, and covering them all is beyond this review's scope. Of all the mentioned techniques, water-splitting utilizing solar energy is the cleaner, most excellent efficient and one of the most promising method.^{7,8} This method imitates naturally occurring photosynthesis in which plant leaves capture solar photons and then break water molecules and store them as chemical energy. Similarly, in this artificial system, semiconductor material (with suitable bandgap) acts as a leaf to capture irradiated photons and use them for water molecule breaking. Water-splitting is a surface phenomenon in which molecule breakage ($H_2O(aq.) \rightarrow H_2(g) + O_2(g)$) happens at the surface of the semiconductor. Briefly, whenever solar light falls onto the photocatalyst surface with an incident energy of $h\nu \geq$ bandgap of the semiconductor will result in energy absorption and generates pair of excited electrons and holes. These exciting charges are responsible for OER and HER reactions. This water-splitting method can be classified as photocatalysis (PC) and photoelectrochemical catalysis (PEC).

The only fundamental difference between the two is that PEC utilizes a three-electrode assembly, an external biasing source

followed by a solar source, and PC uses only solar light. PC seems to be the most economical and easy method in which powdered photocatalyst is mixed with water and then exposed to sunlight. Still, this process undergoes severe limitations, i.e., higher bulk recombination, faster activity equilibrium and scalability constraint, making the system inefficient.⁹ On the other hand, PECs efficiency highly depends upon catalyst activity and interfacial charge transfer kinetics.^{7,10–12} The reaction pathways of photoelectrochemical water splitting are:¹³



These reactions are endothermic because water is one of the most stable forms of hydrogen.^{12,14,15} The primary limitation of this method is that it is still at the lab scale and lacks affordable, efficient and durable semiconductors.

It is worth mentioning that photocatalyst-specific review articles are abundant, but most don't discuss the selection and engineering aspects. In this context, we are trying to bridge it by primarily focusing on strategies related to catalyst designing, designed system analysis, and its implementation towards greener commercially viable technology trends. This article mainly focuses on the conceptual approach helpful for budding researchers in the fascinating area of research in PEC. It can also help to incubate some more feasible ideas for quality research.

Aspects of Photo-Electrode Designing and its Fabrication

Band structure.—In the case of photo-electrochemical water-splitting, when semiconductor photo-electrode is submerged in the electrolyte, the majority of charges (e^- in n-type and h^+ in p-type semi-conductor) start migrating towards the interface resulting in the development of the depletion region (or space-charge region) & soon will attain thermodynamic equilibrium. This charge diffusion will result in a built-in potential barrier to resist further charge transfer. Hence, band bending is observed at the boundary (n-type: upwards and p-type: downwards); & it is represented in Fig. 2. These charge separations are responsible for generating photocurrent and diode

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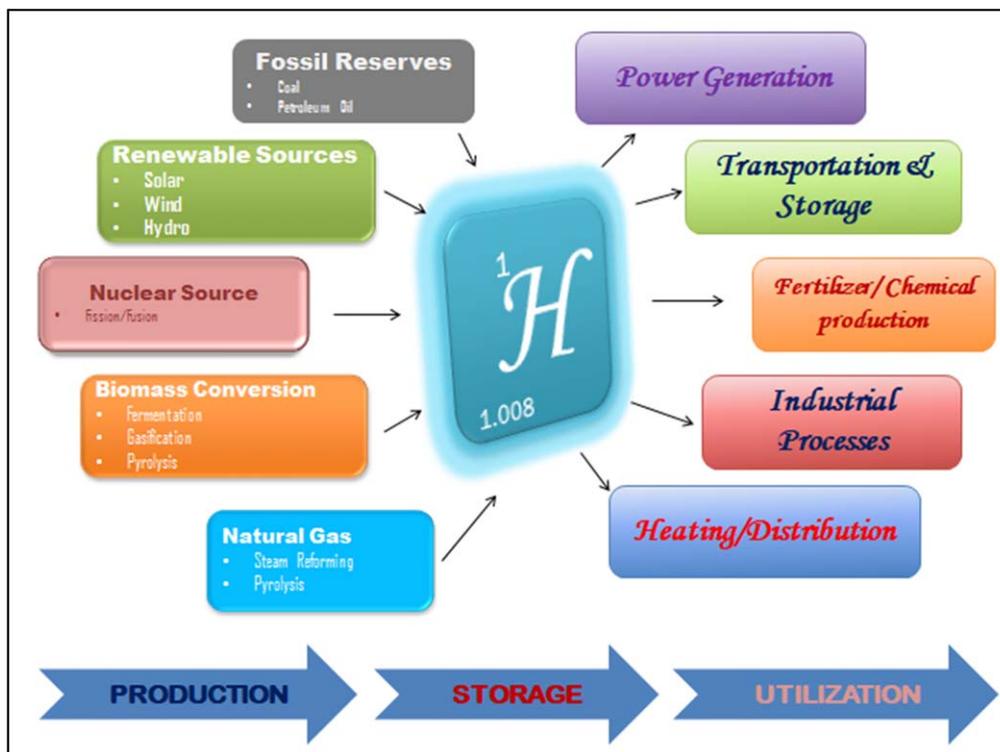


Figure 1. Representation of various hydrogen generation routes available.

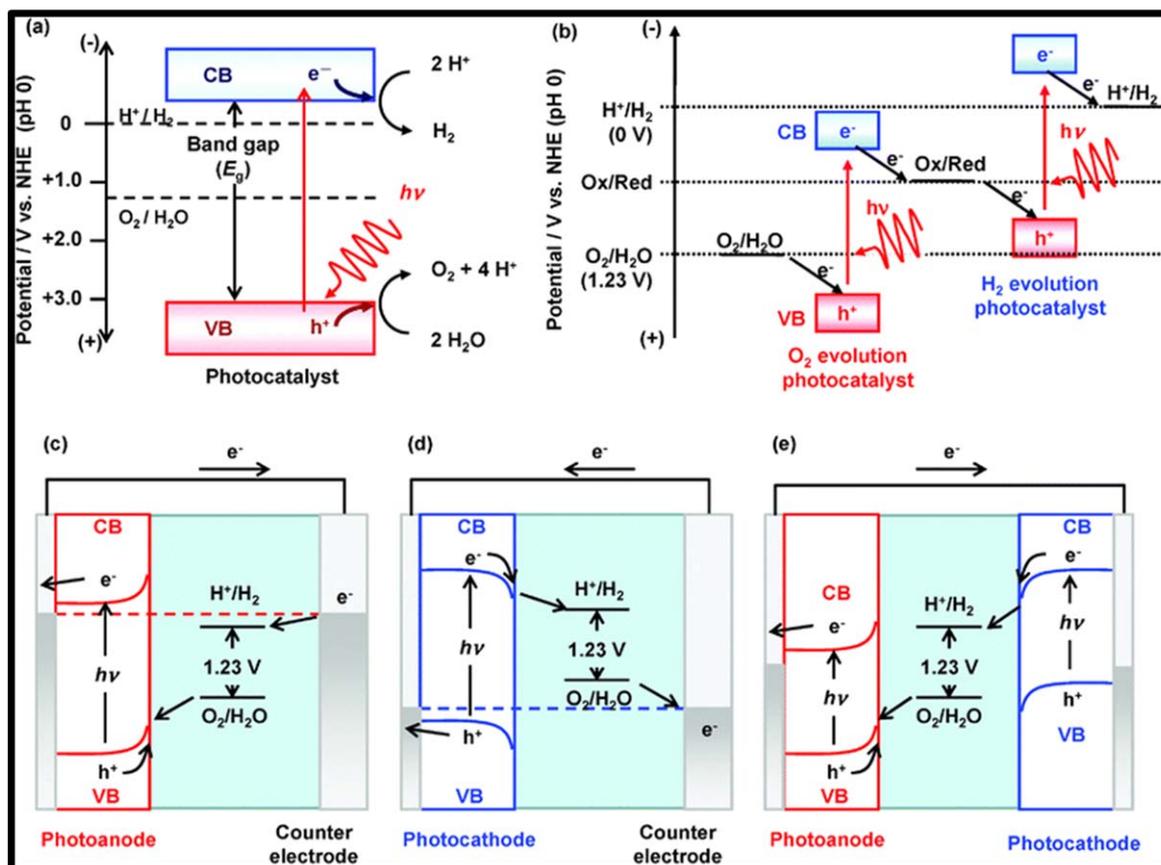


Figure 2. Graphic visualization of PEC energy diagrams for (a) photoanode; (b) photo-cathode, and (c) Z-scheme outline (Adapted with permission from Ref. 16).

effects under illumination conditions.¹⁶ Therefore, selecting materials with smaller bandgaps is essential for improved system performance.

Characteristics of suitable substrate & its fabrication methods.—The performance of any photoelectrode primarily depends upon the variety of substrate, deposition thickness, and the modification technique used. The substrate selected for the photo-catalyst must be conductive to attain faster charge conduction at the semiconductor/electrolyte edge. Some of the available substrates for the PEC study are Au, stainless steel, Si, ITO (Indium Tin oxide coated glass), FTO (Fluorine-doped ITO glass) and others.^{17–19} The next most crucial aspect is the thickness of deposited photocatalyst thickness; it determines the rate of photo-charge generation and delayed/suppressed recombination rates because ion penetration depth has an inverse relation with its consistency.

The material falling under the direct-band gap semiconductors (e.g. GaAs, InAs, InSb, GaN, InN, ZnO, CdSe, etc.) have absorption coefficient $\alpha \sim 10^6 \text{ cm}^{-1}$ thickness of one micron is sufficient.^{20,21}

On the other hand, indirect bandgap semiconductors (Si, Ge, GaP etc.) have $\alpha \sim 10^4 \text{ cm}^{-1}$, and a width of some hundred microns will be sufficient.²² It may be because, with the increase in thickness, the ohmic resistance of the system also increases, resulting in depleted performance.^{23,24} The controlled thickness and the precise morphological orientation of the photocatalyst strongly affect the overall system efficiency. Hence, one needs to be extra careful in it. Among various available techniques, constraints of fabrication cost and desired orientation are always the decisive factors. For instance, if it requires a pure single crystal for the application, then the molecular beam epitaxial (MBE) system is chosen regardless of its cost factor.²⁵ Similarly, for better thickness control for thin films, atomic layer deposition (ALD) is suggestible.²⁶

Efficient catalyst designing strategy.—The electrode design includes various engineering aspects, i.e. morphological tailoring, bandgap engineering, interfacial chemistry, the electro-catalytic activity of the species, solution (electrolyte) resistance, or charge

transfer electrochemistry, as presented in Fig. 3. Hence, clubbing all the mentioned species and looking into only one material is barely possible; therefore, one or more than one different suited semiconductor was brought together to meet all desired expectation(s).²⁷

It is a growing research area to make hydrogen economy possible someday. Trending design schemes in literature are (i) Increasing catalyst loading per unit of the electrode (by Nano-patterning or improved surface engineering) and (ii) empowering each active site of the catalyst to improve photo-catalysis. However, cumulative physical stacking can (theoretically) improve semiconductor conversion rate but might restrain other performance parameters (e.g. interfacial electrochemistry and others). On the other hand, when the intrinsic activity of each active site of the catalyst is improvised, then without increasing the geometrical surface area of the working electrode, its electrochemical performance can be boosted up to 10 folds.^{28,29} Generally speaking, the second approach is cost-effective and results in efficient catalyst design. This section aims to deliver a vision about selecting a few essential properties insufficient to design a catalyst with utmost activity.

Nano-Structuring facet.—In the designing phase, Nano-scaling brings various appreciable advancements in system performance and certain limitations in the form of losses. These are³⁰

1. reflection loss causing poor light absorption,
2. recombination loss resulting in poor interfacial kinetics due to less number of charged ions, and
3. Photo-corrosion loss results in active layer depletion and lower band bending, originating from half-done electrochemical performance.

All of them are discussed briefly here, along with suggestible reported design strategies.

(i) **Reflection losses:** Any material absorptivity is evaluated using Beer–Lambert’s law.²⁷ Suppose the semiconductor material has a flat surface and higher refractive indices. In that case, the maximum volume

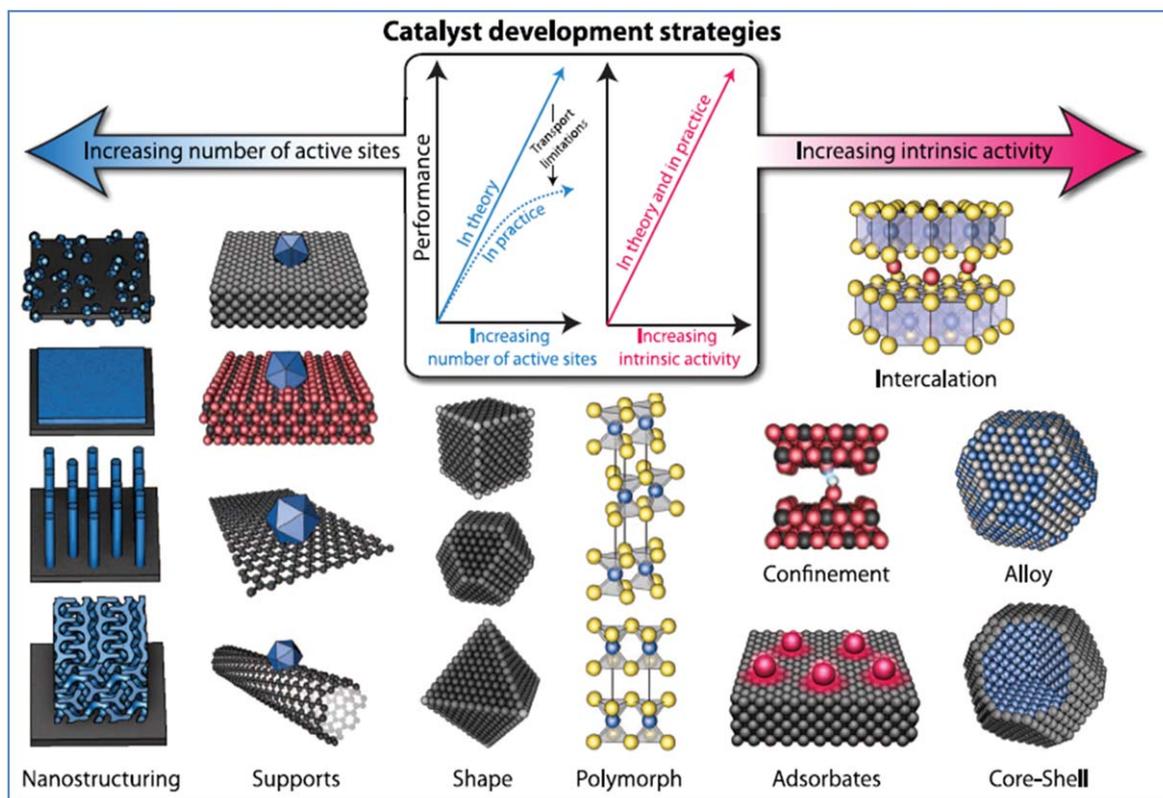


Figure 3. Schematic representation of various catalyst designing morphologies (Adapted with permission from Ref. 28).

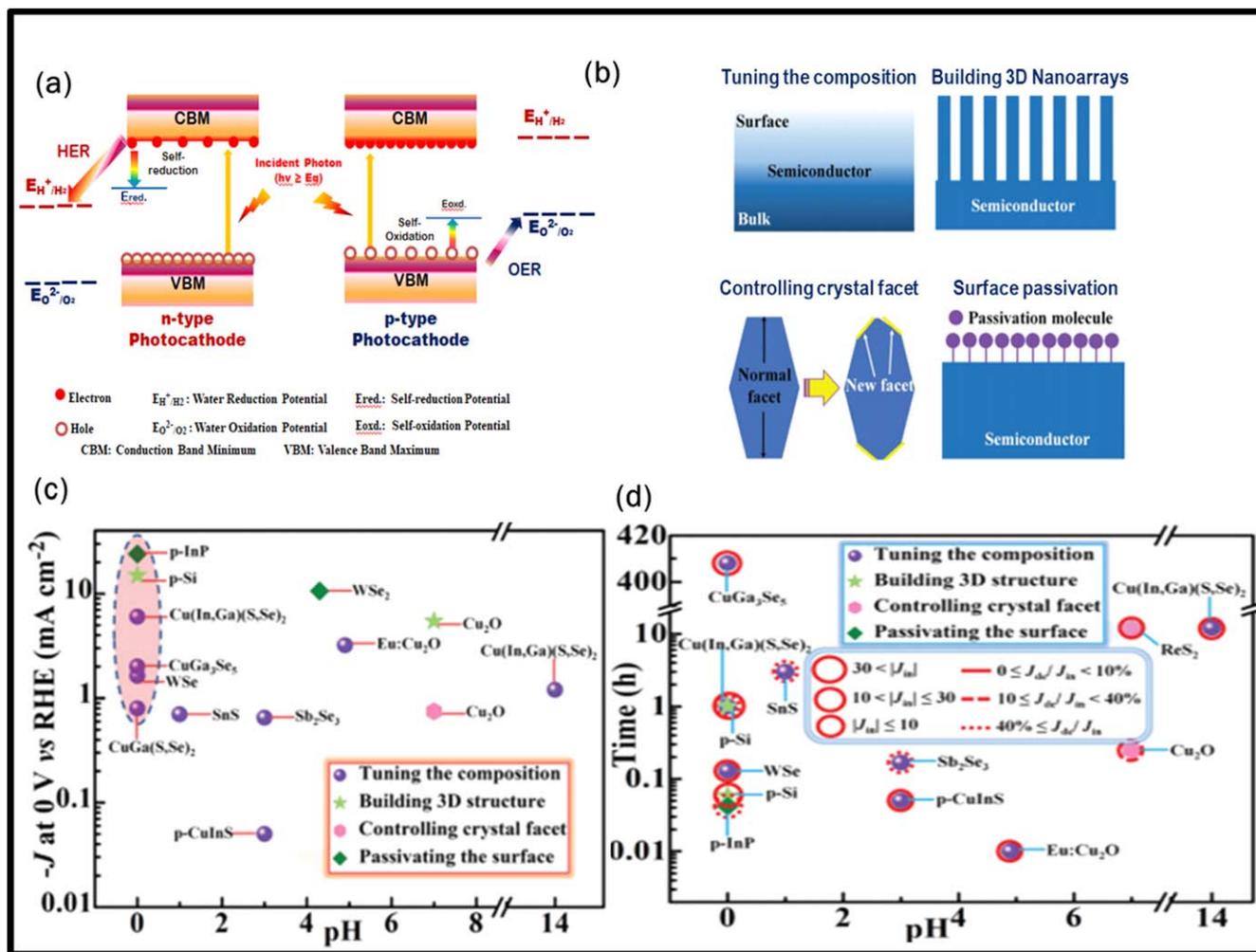


Figure 4. Schematic representation of photo-cathode (a) instability mechanism at band-alignment, (b) surface modification schemes, (c) recent advancements in photo-cathodes and (d) its stability (Adapted with permission from Ref. 63).

of solar-spectra is unused due to direct reflection(s).³¹ It is evident that a semiconductor with thickness ≥ 2.5 of its penetration depth (α^{-1}) & darker in colour, predominantly black (e.g., black titania), reports higher absorptivity.^{30,31} Generally, surface eroding is applied to counterbalance this loss since it forms multiple active sites, causing numerous internal reflections. Besides, nanostructures such as nanowires, nanorods, and nanotubes possess different charge transfer mechanisms providing a low interruption path to photo-generated ions.³²

(ii) **Recombination losses:** The created photo-ions drift from bulk to the surface of the semiconductor to complete the preferred redox mechanism. Ideally, all charges have to reach the redox site. Still, maximum charges recombine as soon as they are formed. The rest headed towards the surface undergoes during or after reaching the surface (already discussed in the photo-catalysis section). Therefore, it is desirable to either wipe off any charge or create a delayed time in recombination; carbon supports (Graphene, CNT, and fullerene) within the catalyst can suppress such recombinations.^{33,34} This support layer acts as a scavenger, which absorbs one type of charged ion (either electron or hole) and then re-emits it after a short delay; this delay helps to get populated charges at the surface for HER/OER, respectively.³⁵ These carbon supports can be in nano-coating,³⁰ co-catalyst,^{19,36–38} and base support for decorated with nano-structure,^{39–41} core-shell heterostructures,^{42–44} noble metal quantum dots as well.^{45–50}

(iii) **Photo-corrosion losses:** In the electrochemical cell, when the active semiconductor surface is irradiated with solar light, the generated charged ions undergo undesirable but thermodynamically viable reaction resulting in self-oxidation and -reduction at the surface,

resulting in depletion of the active layer, this surface phenomenon is photo-corrosion.⁵¹ Based on the simulation studies, for water-splitting application, it is evaluated that the stability of the photo-electrode is decided by the band-alignment of the electrode material w.r.t water oxidation (or reduction) potentials as presented in Fig. 4. In other words, when the self-oxidation potential (E_{oxd}) of the n-type photo-anode is lower (i.e. more positive) than water oxidation potential (E_{O_2/H_2O}), then induced holes will erode the semiconductor surface, similarly if self-reduction potential (E_{red}) of the p-type photocathode is higher (more negative) than water reduction potential (E_{H^+/H_2}) then photo-electrons results in electrode depletion.⁵² These losses can be minimized by (i) doping⁵³ or sensitization of the semiconductor for better band-alignment^{47,54,55} (ii) creating 3-D Nano-architecture^{39,56} (iii) morphological alterations or facet modification^{57–59} and (iv) surface passivation by protective coating.^{58–62}

Considering these losses, selecting an appropriate semiconductor is always a crucial and decisive step in any reaction. In PEC, the desired photocatalyst must elevate photo-charge generation, separation, transfer and restrict backreaction during the entire cycle. Based on the response, the possible arrangement could be: (a) For OER: n-type anode and metal as cathode; (b) For HER: n-type cathode and metal as anode and (c) For Z-scheme: n-type cathode and p-type anode.¹⁶

Design experimental study layout.—The performance of any synthesized photocatalyst is studied by using various available characterization techniques enlisted in Table I:

Table I. Showing different characterization techniques suitable for experimental planning.

S. No.	Study parameter	Suitable technique	Justification	Suggestion/Conclusion
1	Bandgap	UV-visible	<ul style="list-style-type: none"> • Provides details about electronic transitions • Material suitability, i.e. $1.5 < E_g < 2.5$ 	<ul style="list-style-type: none"> • The material showing superior bandgap properties might not be suited for photo-electrode. • Consider it as a preliminary test only.
2	Photo-corrosion	Light irradiated Open-Circuit Potential (OCP)	<ul style="list-style-type: none"> • Provides Flat-band potential • Electrical conduction 	<ul style="list-style-type: none"> • Flat-band pot. (U_{fb}) > redox pot. of H^+/H_2 couple for water splitting. • Photo corrosion may occur. • Recombination rates must be small to get flattened band easily. • Data obtained is complicated to interpret for non-ideal samples
3	Charge-carrier density	Mott-Schottky	<ul style="list-style-type: none"> • Flat-band potential (U_{fb}) • Charge-carrier density • Electrical conduction • Doping concentration 	<ul style="list-style-type: none"> • The resistivity of the model must be known to get good results
4	Electrode characteristics	Cyclic voltammetry (In the presence and absence of light)	<ul style="list-style-type: none"> • Photo-current(sat.) density • Photo-current generation range • Flat-band potential (U_{fb}) 	<ul style="list-style-type: none"> • Catalyst can help to lower or reduce the over-potential range. • Photo corrosion sometimes happens during this study.
5	Efficiency	IPCE, ABPE, STH	<ul style="list-style-type: none"> • Band-gap • Photocurrent generation efficiency 	<ul style="list-style-type: none"> • The value may vary if the light source makes different photon numbers at a particular wavelength. • The system may show overshoot in IPCE may be due to photo-corrosion Faradic efficiency (η_F) must be accurate, or true STH might not be obtained.
6	Gas generation identification	Gas Chromatography	<ul style="list-style-type: none"> • Faradic efficiency can be obtained 	<ul style="list-style-type: none"> • The reaction vessel must be adequately sealed for correct results.

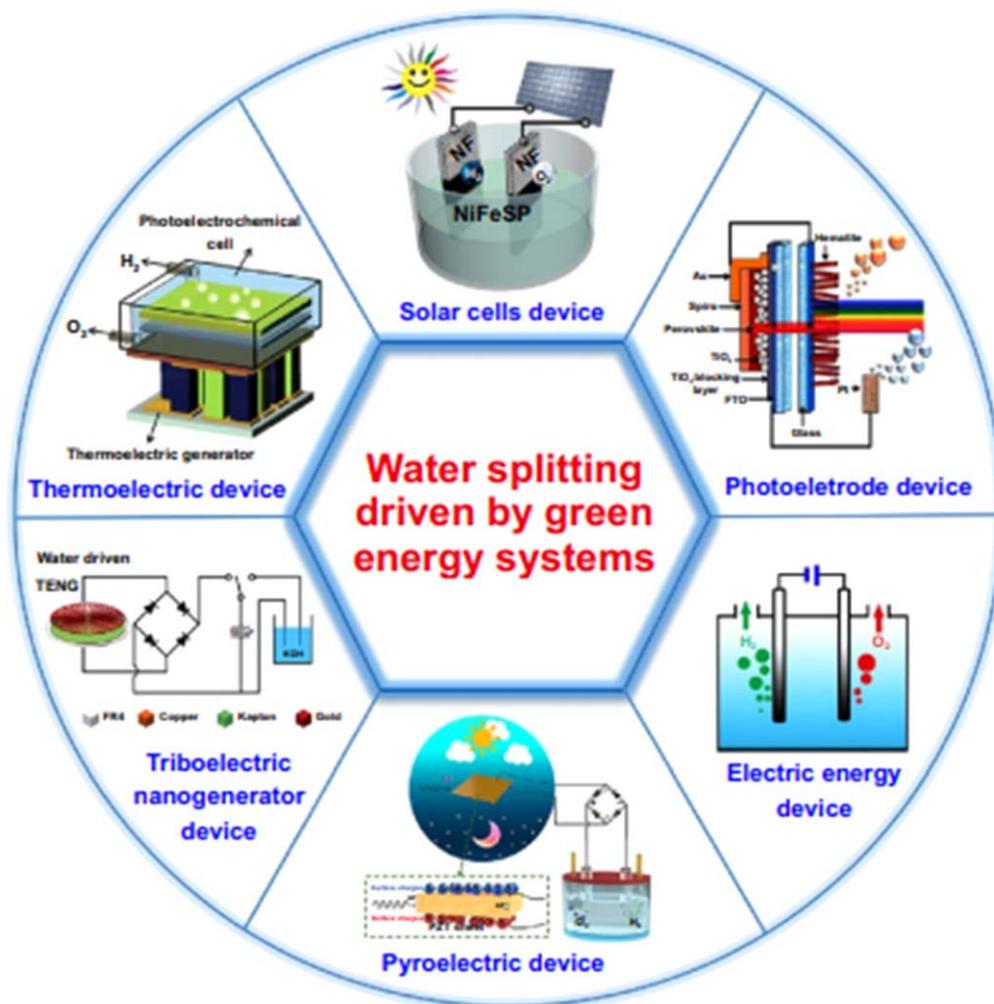


Figure 5. Schematic visualization of various green PEC system designs (Adapted with permission from Ref. 64).

The performance of any synthesized photocatalyst is studied by evaluating the efficiency of the system as enlisted in Table II.¹

Advances in Water Splitting Devices for Hydrogen Generation

Various prototypes are at the baby stage in terms of real-time system designing strategy toward a hydrogen economy. Still, multiple innovations towards device development have been reported recently, utilizing simple yet effective energy sources such as solar, wind, mechanical rubbing, and thermocouple type orientations, respectively. Systems such as electrolyzer, TE, TENG, pyroelectric, and solar-cell driven PEC devices are discussed and presented in Fig. 5. In this section, we are trying to cover all possible system-related aspects and separate limitations and challenges.

Photo-electrode devices in tandem cell arrangement.—*Tandem cell* or *Z-scheme* arrangement refers to complete water-splitting, i.e. simultaneous HER & OER. Theoretically, the potential of 1.23 V is a prerequisite to make the splitting process thermodynamically feasible. Though, in practical systems, usually higher voltage is demanded to overcome the hurdle of electrode over-potential, which is provided externally. Hence, to cut this surplus electricity demand, the utility of such tandem arrangement(s) will turn photocurrent generation within the system to meet this driving energy demand.^{65,66} In this context, continuous improvements are going on from 2% STH⁶⁵ to 20% STH using perovskite and III-V semiconductor family.^{67–70} This design strategy is standalone and

feasible for practical utility, but presently it is struggling due to restraint of poor efficiency, sophisticated equipment, and lowest defect tolerance.⁷¹

Electric energy devices.—An electrochemical cell is created in electro-potential series, which will help establish an ohmic contact between the electrodes via ionic charge present in an aqueous electrolyte. It is an externally-driven mechanism in which electricity is supplied through the electrodes to trigger non-spontaneous reactions, i.e. water splitting. Based on cell design and type of chamber/membrane used, this can be classified as alkaline; polymer-electrolyte membrane and solid-oxide, respectively, as tabulated in Table III. In alkaline electrolysis, electrodes are submerged into a liquid electrolyte prepared by NaOH/KOH salt, and gas evolution at the electrode is visible once an electric current passes through it. In polymer-electrolyte membrane electrolysis, porous electrodes are mounted onto the polymeric membrane (usually Nafion), known as MEA (membrane electrode assembly); it provides a better H₂ generation rate due to suppressed recombination rate and lower resistance path.⁷² It was initially employed in the fuel-cell application and later explored for water-splitting.

Nevertheless, the only limiting condition is high production cost because expensive noble metals (Pt for Hydrogen and IrO₂ for Oxygen evolution) are used as catalysts. However, this limitation may be countered in solid-oxide electrolysis (also known as high-temperature electrolysis). Industrial waste heat expelled through giant heat sinks is utilized to produce large-scale hydrogen production.^{72–75}

Table II. Representing types of reported efficiencies in PEC analysis.

	ABPE	IPCE	STH	APCE
1	It provides efficiency in terms of photo-response of the photo-electrode	It provides efficiency in terms of photon energy (i.e. ratio of photons absorbed to photons incident)	It provides efficiency in power (i.e. power output to power input).	It provides efficiency in terms of absorbance characteristics of the material (i.e. no. of photo-carrier generated by each photon falling on the substrate)
2	It is dependent upon the amount of voltage applied between WE and CE	It is independent of the type of photon source unless no. of the incident photon is the same at each wavelength (e.g. if photons at 400 nm = photons at 600 nm, then it gives the same IPCE value).	It is sensitive toward calibrated broad-spectrum solar energy (AM 1.5 G source is used frequently)	It absolute losses generated due to incident photon reflection from the surface. It is simply IPCE calculated by subtracting interfacial or kinetics losses in the system.
3	Voltage is applied between WE and CE.	External applied biased voltage is allowed between RE and WE	A compulsory zero-bias condition is necessary between WE and CE.	NA
4	It provides system performance but is not true STH	It provides maximum STH value over the entire spectral band (at no applied bias)	It provides actual efficiency of the system.	It provides system performance
5	NA	Equivalent to External Quantum Efficiency (EQE)	It provides actual efficiency of the system.	Equivalent to Internal Quantum Efficiency (IQE)
6	Calculated by photocurrent measurements with applied potential	Calculated by photocurrent measurements with applied potential under monochromatic light	2-Electrode zero-bias photocurrent method is applied	Calculated by UV-visible spectroscopy.
7	$ABPE = \left[\frac{[j_{ph} (mAcm^{-2}) \times (1.23 - V_b)(V) \times \eta F]}{P_{total}(mWcm^{-2})} \right]$	$IPCE = EQE = \frac{[j_{ph} (mAcm^{-2}) \times 1239.8(nm \times V)]}{P_{mono}(mWcm^{-2}) \times \lambda(nm)}$	$STH = \frac{[j_{sc} mAcm^{-2} \times (1.23V) \times \eta F]}{P_{total}(mWcm^{-2})}$	$APCE = IQE = \frac{IPCE}{(\eta)}$

(Where, P_{Total} = Incident power density from solar illuminator; j_{sc} = Short circuit current density; η_F = Faradic Efficiency; j_{ph} = Photon current density, V_b = Applied biasing voltage; η = absorbance (Generated charge carriers per incident photon flux).

Table III. Types of electrolysis and its working chemical equations and optimized working temperature ranges.

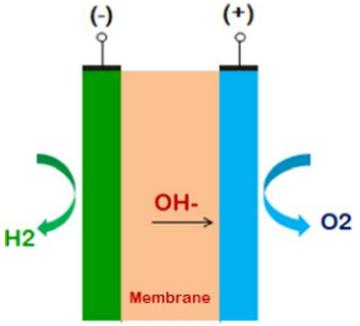
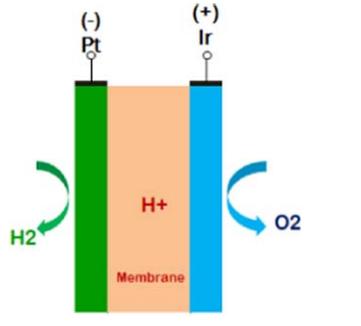
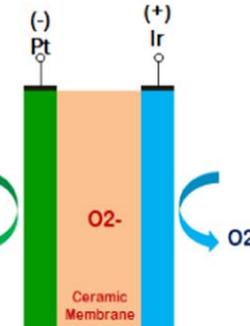
Parameters	Description		
	Alkaline	Membrane	High temperature
Types of electrolysis:			
Anodic reaction:	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O$	$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+$	$H_2O \rightarrow \frac{1}{2}O_2 + 2e^-$
Cathodic Reaction:	$H_2O + 2e^- \rightarrow 2OH^- + H_2(g)$	$2H^+ + 2e^- \rightarrow H_2(g)$	$H_2O + 2e^- \rightarrow O^{2-} + H_2$
Transport ions:	OH^-	H^+	O^{2-}
Working Temp. array:	40 °C–90 °C	20 °C–100 °C	700 °C–1000 °C
Schematic diagram:			

Table IV. Representing a comparison between types of pyro material based PEC systems.

S. No.	Parameter	Internally-positioned pyro-material	Externally positioned pyro-material
1	Position of pyro-material	Suspended in the electrolyte in particle form	Externally placed
2	Gas separating chamber	Not present	OER and HER occur at two different electrodes. Therefore, not required
3	Efficiency	Low	High
4	Conversion due to	pH variation	The rectifier circuit is used to convert supply and directly applied across cathode and anode to perform HER & OER simultaneously.
5	Data available	Simulation and experimental	Experimental

Pyroelectric driven PEC devices.—It could be an endless energy-producing source in which transient voltage is induced because of temperature ($dT/dt \neq 0$) variation applied on the crystal facet.^{76–78} This phenomenon is merely visible in the materials having polar crystal symmetry (called non-centrosymmetric materials). These are the subclass of piezoelectric materials with a slide change in input stress (i.e. mechanical stress or temperature variation stress).⁷⁸ To create energy alternatives, waste heat excreted from the industrial sector could produce endless electricity that could be stored or used directly. In pyroelectric driven PEC systems, as tabulated in Table IV, the thickness of and surface area of the pyro material affects the induced voltage across the crystal because it alters the atomic orientation of the FCC crystal temporarily.⁷⁶

Triboelectric Nano-generator (TEng) based PEC systems.—TEng is a current hot topic of research for developing standalone or self-powered PEC devices. The word triboelectric is derived from a Greek word that means electricity produced due to rubbing or friction.⁷⁹ In structure, two rubbing materials (dielectric-dielectric or metal-dielectric layer) are connected with electrical contacts and insulations (between the layers). As one layer slides over the other (back and forth), it will disturb the static charge layer (at rest) and create a potential difference between the electrodes. This mechanism helps generate AC signals that were further converted to DC signals using a rectifying circuit headed towards storage and provided to electrodes in the PEC system.⁸⁰ In practice, the device type, schematic construction, material selection, and respective combinations used by various researchers are visualized in Fig. 6.

Thermoelectric (TE) device based PEC.—These devices utilize the hot-cold temperature variation principle, formerly called the See-back

Effect. In brief, a pair of materials form a two-terminal thermocouple in these systems. One is termed a hot junction (where temperature elevation is implied) and the two-terminal thermocouple. One is termed a hot junction (where temperature elevation is indicated). The cold junction (kept at an ice-bath) temperature gradient creates potential difference and makes electrons flow. In recent advances in standalone system advancement, hybrid TE devices are grasping lamp light attention from researchers worldwide. This hybrid-TE consists of TE-coupled with piezoelectric material to enhance performances towards energy conversion, i.e. thermal to electrical energy,^{81,82} as presented in Fig. 7. In context with solar light utilization, hybrid-TE might be very promising because commercially available TE was covered with semiconductor materials (narrow & wide band-gap) and group VIII metals, showing absorption towards an ultra-violet band of the spectrum.^{83–85}

Solar-cell devices based on PEC devices.—In the fully solar-driven assembly, solar cells and panels are connected in series so that maximum energy storage and utility can be assured.⁸⁶ As shown in Fig. 8, various types of available solar cells, e.g. CIGS (copper Indium Gallium Selenides) solar cells,^{87–89} DSSC (Dye-sensitized solar cells),^{90–92} perovskite solar cells^{91,93,94} and others^{95–97} are used by various researcher to provide STH up to 30%.^{98–100}

Conclusion and Future Scope

In recent times, green routes toward water splitting have made considerable developments. They soon will be able to achieve a scalable, practical solution toward solar-driven clean energy sometimes more quickly. Although, such systems suffer from severe challenges, including:

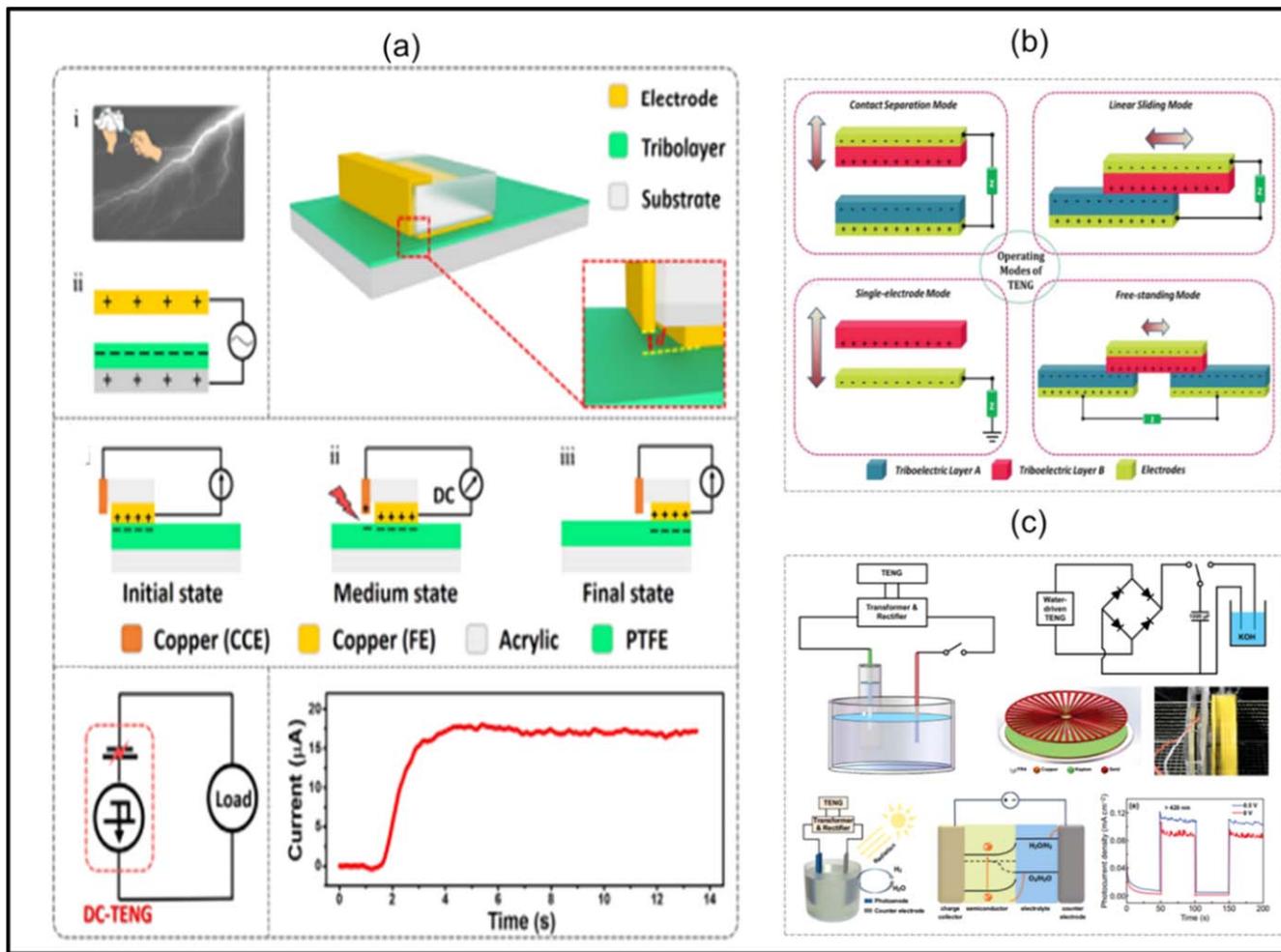


Figure 6. Representation of TENG-PEC system (a) working principle, (b) operating modes, and (c) Au-decorated TiO₂ photoelectrode (Adapted with permission from Refs. 64, 79, 80).

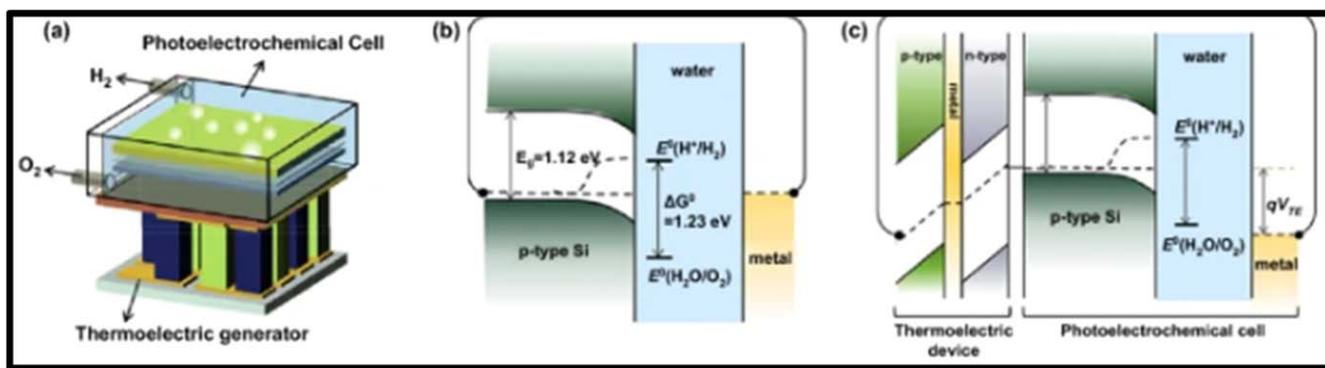


Figure 7. Representation of TE-PEC system (a) working principle, (b) energy level diagram for PEC system and (c) PEC-TE (Adapted with permission from Ref. 83).

- (i) highly stable, active and economically viable photocatalyst. It is essential to understand that non-noble metal-based tandem photocatalyst works well in alkaline media but suffers limitations in acidic ones and vice-versa.
- (ii) photo/electrocatalysts lack to fulfil the high current-density demand for industrial applications and lasting electrode stability.
- (iii) utilizing the PV/TE/pyroelectric/TENG based devices to generate electrical signals to run the water-splitting increases the cost of hydrogen production.

This review aims to give a complete essence of experimental aspects (from planning to calculations), which could act as a handbook guide for scientists, especially early researchers in this field. It will also provide a vision for new catalyst designs to address purely green PEC systems. In view of superior charge-transfer characteristics, and low production cost, organic semiconductors are ideal for PEC hydrogen production. Organic photoelectrochemical devices (i.e. OPEC) have opened a new set of possibilities in recent times because they can provide high photo-voltage and pair highly conducting donors (PEDOT: PSS, BPhen, BDD-TT) with acceptors

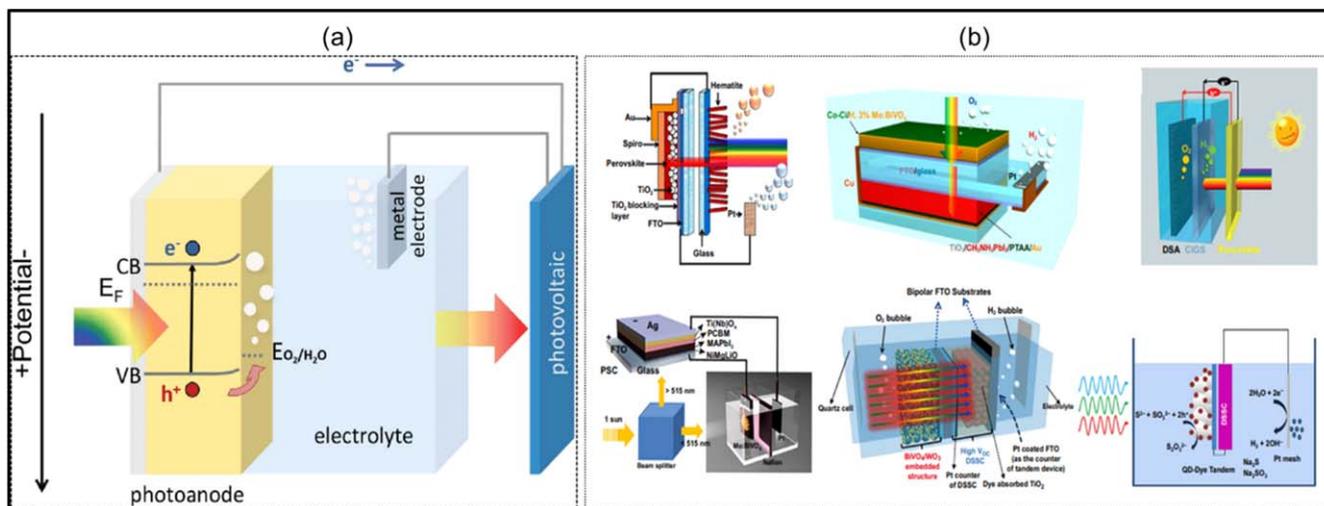


Figure 8. Representation of PV-PEC system (a) working principle, and (b) device designs (Adapted with permission from Refs. 65, 99).

based on fullerene free structures. These may bring a revolution in PV assisted tandem PEC devices and multijunction solar cells. However, organic-semiconductor-based photoelectrodes have not been extensively explored for PEC water-splitting because of their low stability in water. Furthermore, the compilation of innovative PEC devices possibly will lead to tactics such as unsupported cell scheme and tandem absorber arrangement that could mend the system's overall efficiency. With continued improvement in PEC devices, it is apparent that the hydrogen economy will see the light of day soon.

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