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Sunlight harvested: A historical evolution of materials for photovoltaics, solar fuels, photocatalysis, and emerging light-charged devices

Abstract. *This review treats sunlight as a central driving resource for sustainable technologies and analyzes how materials have been developed to capture, convert, and store solar energy in distinct yet related functional pathways. A historically grounded and cross-disciplinary framework is applied to four main classes of sunlight-driven processes: conversion of solar radiation to electricity, storage of solar energy in chemical bonds, photocatalytic degradation of pollutants, and direct light-assisted energy storage. The evolution of photovoltaic systems is examined from crystalline and multicrystalline silicon to thin-film absorbers, dye-sensitized and organic solar cells, and contemporary metal halide perovskites and tandem configurations, with emphasis on the interplay between efficiency, stability, and material availability. Photoelectrochemical and catalytic routes to solar fuel production are analyzed with specific attention to the development of metal oxides, molecular complexes, nanostructured catalysts, and selective* CO_2 *reduction systems as platforms for storing sunlight in chemical bonds. Photocatalytic environmental remediation is considered in the context of semiconductor design, interfacial charge-transfer processes, and the integration of light-harvesting materials into water and air treatment schemes. Recent advances in light-charged and photo-assisted energy storage, including photo-batteries, photo-supercapacitors, redox-based solar energy storage concepts, and photo-responsive concentration cells, are evaluated as emerging approaches that seek to couple photon absorption, charge separation, and storage within unified device architectures. Across these domains, the study identifies recurrent materials design principles, including band gap and band alignment optimization, catalyst coordination environment, interfacial and kinetic control, operational durability, reliance on abundant and low-toxicity elements, and life-cycle compatibility with large-scale deployment. By comparing these trajectories within a single analytical framework,* *the work delineates common patterns of technological success and failure and defines realistic directions for the rational development of adaptive molecular, hybrid, and semiconductor materials for next-generation sunlight-driven energy and environmental technologies.*

Keywords: *materials history; photo-assisted energy storage; light-harvesting materials;* CO_2 *reduction; sustainable materials design*

1. Introduction.

Physically, solar radiation represents the dominant primary clean energy flux at the Earth's surface (Chu & Majumdar, 2012; Lewis & Nocera, 2006).

Technologically, it underpins a broad range of concepts that seek to generate electricity, store energy in chemical bonds, drive redox transformations, and remove pollutants without additional carbon-intensive inputs (Ardo et al., 2018; Fujishima & Honda, 1972; Hoffmann, Martin, Choi, & Bahnemann, 1995).

Treating sunlight explicitly as this common locomotive allows different materials-based approaches to be viewed within a single framework rather than as isolated thematic fields (Lewis, 2007).

From a historical perspective, four principal sunlight-driven transformation pathways have crystallized into distinct research and technology domains. The first is the direct conversion of solar radiation into electricity in photovoltaic systems (Fig 1. a) (Su, Zhang, Lai, Feng, & Shi, 2010), which traces back to the first observation of the photovoltaic effect by Edmond Becquerel in 1839 (Bulavko, 2024). The photovoltaic effect refers to the generation of an electromotive force and electric current in a material upon exposure to light, as originally observed by Edmond Becquerel in an electrochemical cell. It is distinct from the photoelectric effect, demonstrated by Heinrich Hertz in 1887, which involves the emission of electrons from a surface irradiated by light of sufficient energy. Both phenomena are rooted in the quantum nature of light-matter interaction, yet the photovoltaic effect specifically entails charge separation and current generation within a device, which became the physical basis for solar cell technology. The first practical silicon p–n junction devices at Bell Labs in 1954 (Chapin, Fuller, & Pearson, 1954) then translated this principle into a working power source.

The field subsequently expanded through thin-film absorbers and into organic and molecular approaches. The first efficient planar heterojunction organic solar cell was reported by Tang in 1986, using a CuPc-perylene bilayer architecture (Tang, 1986). The bulk-heterojunction concept was enabled by the discovery of ultrafast photoinduced electron transfer from conjugated polymers to fullerenes in 1992 (Sariciftci, Smilowitz, Heeger, & Wudl, 1992) and implemented in high-efficiency polymer-fullerene devices in 1995 (Yu, Gao, Hummelen, Wudl, & Heeger, 1995).

A parallel molecular pathway arose with dye-sensitized solar cells introduced by O'Regan and Grätzel in 1991 (O'Regan & Grätzel, 1991).

In the past decade, metal-halide perovskites emerged from sensitized cells to solid-state and meso-superstructured architectures, beginning with the 2009 JACS report of perovskite sensitizers (Kojima, Teshima, Shirai, & Miyasaka, 2009) and followed by solid-state devices in 2012 that rapidly achieved near-10% efficiency (Kim et al., 2012; Lee, Teuscher, Miyasaka, Murakami, & Snaith, 2012), ultimately leading to today's perovskite and perovskite-silicon tandem configurations.

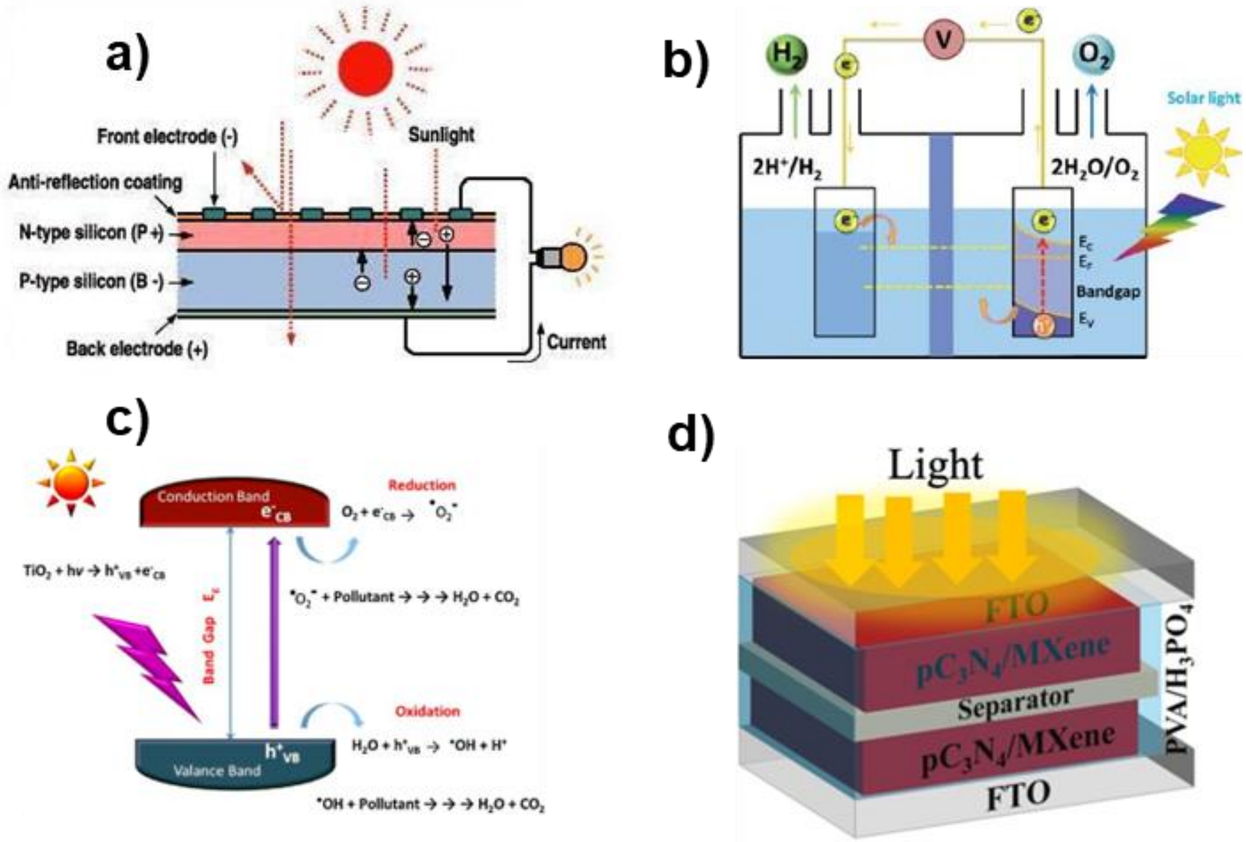

Figure 1. Principal sunlight-driven transformation pathways: (a) photovoltaics (Su, Zhang, Lai, Feng, & Shi, 2010); (b) solar fuels (Bhatt & Lee, 2015); (c) photocatalytic remediation (Wei, Wu, Meng, Zhang, & Cao, 2023); (d) light-charged storage (Kumar, Mondal, Panwar, Shekhawat, & Misra, 2024).

The second pathway concerns the storage of sunlight in chemical bonds through photoelectrochemical and photocatalytic processes for water splitting and carbon dioxide reduction (Fig.1. b) (Bhatt & Lee, 2015). The modern field originates with the demonstration of water splitting on TiO_2 photoanodes by Fujishima and Honda in 1972, which established semiconductor photoelectrochemistry as a route to solar fuels (Fujishima & Honda, 1972). Subsequent progress included integrated devices that couple light absorption with electrolysis, notably the monolithic photovoltaic photoelectrochemical cell for hydrogen production reported by Khaselev and Turner in 1998 (Khaselev & Turner, 1998). Photocatalytic and photoelectrocatalytic reduction of CO_2 emerged soon after the water-splitting breakthrough, with Halmann's 1978 demonstration of photoassisted CO_2 reduction on p-type GaP photocathodes (Halmann, 1978) and the 1979 report by Inoue, Fujishima, Konishi, and Honda showing CO_2

conversion to fuels in aqueous semiconductor suspensions (Inoue, Fujishima, Konishi, & Honda, 1979).

The motivation for these pathways is the production of green hydrogen and solar-derived carbon products that support deep decarbonization targets articulated in international frameworks such as the Paris Agreement and in strategic assessments of hydrogen's role by the International Energy Agency.

Materials development has progressed from mainly UV-active oxides to visible-light-responsive photocatalysts and increasingly selective molecular and heterogeneous catalysts for CO_2 reduction, as summarized in critical reviews of photocatalytic water splitting and solar CO_2 conversion (Chang, Wang, & Gong, 2016; Kudo & Miseki, 2009).

The third pathway concerns the use of semiconductor photocatalysts for the oxidation and mineralization of pollutants in water and air, as well as for self-cleaning surfaces (Fig 1. c) (Wei, Wu, Meng, Zhang, & Cao, 2023). Early proof-of-concept studies demonstrated heterogeneous photocatalytic oxidation of toxic anions such as cyanide and sulfite on illuminated semiconductor powders, establishing titanium dioxide as a benchmark material (Frank & Bard, 1977).

Foundational reviews then consolidated mechanisms and application prospects for TiO_2 photocatalysis across environmental media (Fujishima, Rao, & Tryk, 2000).

The concept of transparent self-cleaning TiO_2 coatings on glass was introduced in the mid-1990s, providing a route to photodegrade organic films directly on surfaces (Paz, Luo, Rabenberg, & Heller, 1995), followed by studies detailing substrate effects and mitigation strategies (Paz & Heller, 1997). Commercialization arrived with photocatalytic self-cleaning architectural glazing, exemplified by Pilkington Activ in 2001, which coupled UV-driven photocatalysis with photoinduced hydrophilicity to enable rain-assisted cleaning.

To expand activity into the visible range, nitrogen-doped TiO_2 and related band-gap engineering approaches were reported in the early 2000s (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001). Subsequent material families, including graphitic carbon nitride, broadened the palette of visible-light photocatalysts and entered environmental degradation studies alongside solar-fuel chemistry (Xinchen Wang et al., 2009).

Standardized assessment protocols for gas-phase depollution, particularly NO and NO_2 abatement on photocatalytic construction materials, were established through ISO 22197 methods and are now widely used in laboratory and field evaluations.

Current research targets include dyes and pharmaceuticals in water, volatile organic compounds and nitrogen oxides in air, and durable self-cleaning or depolluting building surfaces. Reported field deployments show both promise and variability in real-world NO_x reduction, underscoring the need for rigorous kinetics, long-term durability studies, and realistic illumination and flow conditions during performance testing (Dahl, Jensen, Bigi, & Ghermandi, 2023; Russell, Frederickson, Hertel, Ellermann, & Jensen, 2021; Sanchez, Santiago, Martilli, Palacios, Núñez, Pujadas, & Fernández-Pampillón, 2021).

The fourth pathway concerns direct or assisted storage of energy in light-charged devices, where light harvesting, charge separation, and storage are coupled within unified architectures (Fig. 1. d.) (Kumar, Mondal, Panwar, Shekhawat, & Misra, 2024). Foundational proposals that linked illumination to storage appeared in the 1970s (Hodes, Manassen, & Cahen, 1976). Early device embodiments were dye-sensitized photocapacitors, first shown as a two-electrode self-charging capacitor in 2004 and improved with a three-electrode configuration in 2005 (Chen, Yulius, Woodall, & Broadbridge, 2004; Murakami, Kawashima, & Miyasaka, 2005). Integration with battery chemistries followed, including direct solar charging of Li-ion cells and related photo-assisted batteries in the mid-2010s, and fully photo-rechargeable Li-ion operation under ambient light in 2021. Parallel progress in solar flow batteries demonstrated monolithic architectures with double-digit solar-to-output electricity efficiency (Fu, Li, Yang, Lin, Veyssal, He, & Jin, 2021). As an emerging molecular route, a spiropyran based photoelectrochemical concentration cell shows visible-light self-recharging via reversible Zn-spiropyran complexation, illustrating adaptive photochromic chemistry as a viable light-charged storage motif (Hrebonkin & Bulavko, 2025).

Existing literature provides extensive and authoritative reviews within each of these domains. Comprehensive assessments of photovoltaic materials, covering crystalline and thin-film technologies as well as efficiency benchmarks, are given in (Polman, Knight, Garnett, Ehrler, & Sinke, 2016), while the operational principles and performance limits of molecular-sensitizer-based architectures are detailed in reviews of dye-sensitized solar cells (Hagfeldt, Boschloo, Sun, Kloo, & Pettersson, 2010) and organic solar cells (Bulavko, 2024). The mechanistic and materials foundations of semiconductor-mediated water splitting and hydrogen evolution are treated in (Hisatomi, Kubota, & Domen, 2014; Kudo & Miseki, 2009; Walter, Warren, McKone, Boettcher, Mi, Santori, & Lewis, 2010), and the catalytic and computational aspects of CO_2 photoconversion are addressed in (Kovačič, Likozar, & Huš, 2020; Qiao, Liu, Hong, & Zhang, 2014). For environmental applications, foundational and updated accounts of TiO_2-based remediation and surface photochemistry appear in (Hoffmann, Martin, Choi, & Bahnemann, 1995; Nakata & Fujishima, 2012), and the principles and device concepts for integrated photo-rechargeable systems are consolidated in (Pujari, Kim, Abbasi, Lee, Greenham, & De Volder, 2024; Schmidt, Hager, & Schubert, 2016; Yu, McCulloch, Huang, Trang, Lu, Amine, & Wu, 2016). However, these analyses are most often confined to a single technology class or to a narrow subset of materials and performance metrics. They rarely address how different sunlight-driven approaches compete and complement one another, how they rely on overlapping design principles for absorbers, catalysts, and interfaces, or how they collectively translate the same primary solar resource into distinct but interconnected functional outputs. There is also limited systematic discussion of how considerations such as elemental abundance, device stability, end-of-life management, and life-cycle sustainability have historically influenced materials choices across these fields in a comparable manner.

The present study addresses this gap by examining in an integrated way the four transformation pathways in which sunlight acts as the initiating resource: photovoltaic electricity generation, solar fuel production via photoelectrochemical and photocatalytic routes, photocatalytic environmental remediation, and light assisted energy storage. For each pathway, the historical evolution of key materials systems is outlined from foundational demonstrations to state-of-the-art solutions, with emphasis on the scientific and technological conditions under which specific semiconductors, molecular absorbers, catalysts, polymeric and hybrid structures, and interfacial architectures became relevant. Particular attention is given to cross cutting criteria that recur across different technologies, including band gap and band edge alignment with the solar spectrum and target reactions, control of bulk and interfacial charge transport, catalyst coordination environment and active site design, resistance to photochemical and electrochemical degradation under realistic operation, reliance on abundant and non-critical elements, compatibility with scalable manufacturing, and overall life cycle sustainability. Because photovoltaics represent the longest-established and most extensively documented of the four pathways, and because many design principles first articulated for solar cells were subsequently adapted in solar fuels, photocatalysis, and light-charged storage, the photovoltaic section is treated in greater depth and serves as a reference framework for the analysis of the remaining three domains.

Methodologically, this comprehensive review is based on a critical and selective analysis of peer reviewed literature, including seminal experimental reports, landmark conceptual papers, and recent high impact reviews in photovoltaics, electrochemistry, catalysis, polymer and materials science. The discussion incorporates established reference works on dye sensitized and organic photovoltaic systems, photoelectrochemical and photocatalytic solar fuels, and sunlight driven environmental remediation, as well as key contributions on emerging light charged storage concepts. The evaluation is informed by the author’s own research on organic and hybrid photovoltaic devices and on light responsive electrochemical systems, including previous work on the historical development and prospects of organic photovoltaics in a cross disciplinary context (Bulavko, 2024). The approach combines historical reconstruction of key milestones, thematic grouping of related technologies, and comparative assessment of shared materials selection principles and sustainability constraints across the four pathways.

In terms of historiographical orientation, the present study goes beyond a purely chronological listing of milestones. It seeks to identify, at each stage, how the availability of new characterization methods, the shifting priorities of funding agencies and energy policy frameworks, and the interaction between distinct research communities influenced the direction and pace of materials development. Particular attention is paid to episodes in which a technology that appeared promising on efficiency grounds failed to progress because of material scarcity, instability, or incompatibility with manufacturing realities, and conversely, to cases where a seemingly modest material platform achieved dominance through a combination of processability, durability, and cost reduction. This approach allows the historical narrative to serve not only as a record of discoveries but also as an analytical tool for understanding why certain materials design strategies succeeded while others remained confined to the laboratory.

The aim of this comprehensive review is to provide an integrated historical and materials focused assessment of how sunlight has been harnessed as a driving force for green energy and environmental applications, to identify unifying principles that link photovoltaics, solar fuels, photocatalysis, and light assisted energy storage, and to delineate realistic directions for the rational development of adaptive molecular, hybrid, and semiconductor materials for next generation sunlight driven technologies.

2. Sunlight to Electricity: The Photovoltaic Backbone.

Among the four sunlight-driven pathways considered in this review, photovoltaics represent the most technologically mature and widely deployed route from photons to usable energy. The historical evolution of PV materials reflects a recurring tension between efficiency limits, elemental abundance, long-term stability, manufacturability at the terawatt scale, and device architectures that minimize optical and electrical losses. While the portfolio of absorbers and junction concepts has expanded from crystalline silicon to III-V compounds, thin films, dye-sensitized and organic systems, metal-halide perovskites, and multi-junction configurations, only a subset has crossed the threshold from laboratory demonstrator to industrial backbone.

2.1. From the First Silicon Cells to the Silicon Dominance Regime.

The foundational milestones of PV include Edmond Becquerel's observation of the photovoltaic effect in 1839, early selenium and Cu_2O cells in the late nineteenth and early twentieth century, and the breakthrough crystalline silicon p-n junction cell at Bell Labs in 1954 with an efficiency of about 6 % under sunlight (Chapin, Fuller, & Pearson, 1954). These devices established the archetype of a shallow junction in a high purity semiconductor with a built-in electric field for selective carrier extraction.

Over subsequent decades, improvements in crystal growth, dopant and defect control, surface passivation, antireflection coatings, and contact design transformed crystalline silicon from a space technology into the main terrestrial PV platform. Commercial cell efficiencies, which were near 10 to 15 % in the 1970s and 1980s, now routinely reach about 22 to 24 % for industrial PERC, TOPCon, and heterojunction architectures, while best laboratory silicon heterojunction cells approach 27 %, as documented in consolidated efficiency tables. Crystalline silicon offers a near optimal band gap close to 1.1 eV for single junction operation, relies on an abundant and relatively benign element with established production and recycling routes, and demonstrates operational lifetimes of at least 25 to 30 years with modest degradation. At the same time, its indirect band gap requires relatively thick wafers and high temperature processing, and current architectures approach practical limits for single junction performance. This situation has stimulated intensive efforts toward thin film, multi junction, and tandem concepts that can exceed the Shockley-Queisser limit or reduce cost and energy payback time.

2.2. III-V Compounds and the Multi Junction Paradigm.

III-V semiconductors such as GaAs, InP, and their alloys enabled high efficiency single junction and multi junction cells with precisely tunable band gaps and excellent radiative properties. Under one sun, GaAs research cells have surpassed 28 to 29 % efficiency (Green et al., 2025). In concentrator and multi junction configurations, for example GaInP/GaAs/Ge and related stacks with bandgap grading across the solar spectrum, independently certified efficiencies have exceeded 40 % and advanced designs approach the high 40 % range in optimized concentrator systems (King et al., 2007).

These results define the practical upper envelope of photovoltaic performance under realistic conditions and highlight the benefits of spectrally cascading absorbers in multi junction architectures. Historically, however, III-V devices have remained confined to space power and niche concentrator applications. Limitations arise from complex epitaxial growth, high manufacturing cost, and reliance on critical elements such as indium, gallium, and germanium. The III-V trajectory illustrates a general principle that efficiency alone is insufficient if material supply, cost, and large-scale manufacturability are not compatible with terawatt deployment.

2.3. Thin Film Silicon, CdTe, and CIGS: Materials Utilization and Manufacturing.

The drive to reduce material consumption and enable large area, low-cost production led to thin film PV technologies based on amorphous and microcrystalline silicon, cadmium telluride, and copper indium gallium diselenide (CIGS) (Sivasankar, Amorim, & da Cunha, 2025).

Amorphous and microcrystalline silicon (a-Si:H, microcrystalline stacks) use well established, relatively safe chemistries and support flexible or building integrated modules, but suffer from light induced degradation and limited stabilized efficiencies, typically below about 10 to 12 % for commercial modules (Avrutin, Izyumskaya, & Morkoç, 2014).

Cadmium telluride (CdTe) combines a nearly ideal direct band gap of about 1.45 eV with strong absorption, enabling thin absorbing layers and high throughput manufacturing. Best research CdTe cells exceed 22 % efficiency, and commercial modules reach high teens to around 20 %.

Key concerns include cadmium toxicity and the limited availability of tellurium, which require strict process control and closed loop recycling, although life cycle analyses often show favorable energy payback times and competitive carbon footprints.

CIGS offers a tunable band gap in the approximate range from 1.0 to 1.7 eV and very high absorption coefficients. Record CIGS cells surpass 23 % efficiency, with commercial modules somewhat lower (Feurer et al., 2017). However, complex stoichiometry, sensitivity to alkali doping, process uniformity, and dependence on indium and gallium have constrained large scale expansion. Together, CdTe and CIGS demonstrate that thin absorbers with high optical cross sections can reduce material intensity and enable alternative manufacturing routes, but their long-term competitiveness depends on addressing toxicity, resource constraints, and process reproducibility.

2.4. Dye Sensitized and Organic Solar Cells: Molecular Routes and Their Limits.

The introduction of dye sensitized solar cells by O'Regan and Grätzel in 1991 (O'Regan & Grätzel, 1991) established a molecular inorganic hybrid architecture, in which a sensitizer dye absorbs light on a mesoporous TiO_2 scaffold and a redox electrolyte or hole conductor completes the circuit. DSSCs enabled tunable color, semi transparency, and relatively simple low temperature fabrication. Over years of development, co sensitization, cobalt based redox couples, and solid-state hole transport materials pushed record efficiencies to around 13 to 14 % under standard test conditions. Nonetheless, issues with liquid electrolyte volatility, sealing, long term stability, and limited open circuit voltage have restricted DSSCs to niche segments such as building integrated and indoor photovoltaics rather than mainstream power generation.

2.5. Organic Solar Cells.

Organic solar cells based on conjugated polymers and small molecules, progressed from Tang's planar heterojunction CuPc perylene cell in 1986 (Tang, 1986) to bulk heterojunction architectures following the demonstration of ultrafast charge transfer in polymer fullerene blends in 1992 (Sariciftci, Smilowitz, Heeger, & Wudl, 1992). The introduction of non-fullerene acceptors yielded a rapid rise in efficiencies, with certified single junction organic cells approaching about 18 to 19 % (Xuelin Wang et al., 2021). Organic systems offer solution processability, low weight, flexibility, and broad spectral tunability. However, intrinsic and extrinsic degradation under oxygen, moisture, and light, morphology instability, and challenges in large area uniform processing still limit their deployment in long lifetime outdoor installations. As a result, organic PV remains focused on flexible, indoor, portable, and semi-transparent applications. Historically, DSSCs and organic solar cells expanded the conceptual design space for light harvesting and interfacial charge transfer, but did not displace crystalline silicon as the photovoltaic backbone.

2.6. Metal Halide Perovskites, Tandems, and Emerging Multi Junction Architectures.

Metal halide perovskites originated in 2009 as efficient sensitizers in liquid electrolyte cells and quickly transitioned to solid state mesoscopic and planar devices that exceeded 10 % efficiency by 2012 (Lee, Teuscher, Miyasaka, Murakami, & Snaith, 2012). Within little more than a decade, certified single junction perovskite cells have surpassed 26 %, and perovskite silicon tandem cells have exceeded 33 % in two terminal architectures, as documented in standard efficiency charts (Polman, Knight, Garnett, Ehrler, & Sinke, 2016).

Perovskites combine strong absorption, long diffusion lengths, defect tolerant electronic structure, and compositional band gap tunability in a form compatible with solution processing, low temperature deposition, and direct integration on established silicon technologies (Saparov & Mitzi, 2016).

This combination has made perovskite-based tandems the leading candidate for next generation multi junction architectures beyond pure III-V stacks. All perovskite tandems, perovskite on silicon tandems, and other hybrid multi junctions seek to exploit spectral splitting to surpass the single junction Shockley-Queisser limit while leveraging less resource intensive materials and simpler processing. At the same time, the soft ionic lattice of perovskites leads to sensitivity to moisture, oxygen, heat, and electric fields, with ion migration, phase segregation, and interface degradation still limiting operational stability.

The use of soluble lead in most high efficiency compositions raises environmental and regulatory questions, especially for large area deployment, although lead content per watt is low and closed loop strategies are under development.

Thus, perovskites and perovskite-based tandems currently occupy an intermediate status: technologically disruptive in terms of efficiency and architectural flexibility, but not yet fully bankable at the scale and lifetime demonstrated by crystalline silicon. Their future role will depend on sustained advances in stability, encapsulation, scalable manufacturing, and end of life management.

2.7. Efficiency Trajectories, Commercial Reality, and Materials Constraints.

The evolution of record efficiencies across different PV technologies provides a compact historical fingerprint. Crystalline silicon progressed from single digit efficiencies in the 1950s to about 27 % in the best modern cells. CdTe and CIGS advanced from below 10 % to beyond 20 % in optimized devices. III-V multi junction concentrator cells moved from around 20 % to well above 40 %. Metal halide perovskites increased from initial values near 3 to 4 % in 2009 to beyond 26 %. Dye sensitized and organic solar cells, starting from sub one percent prototypes, reached approximately 12 to 14 % and up to about 18 to 19 %, respectively, in advanced architectures. Multi junction and tandem configurations that combine complementary absorbers now define the absolute efficiency frontier in both III-V and perovskite silicon families (Fig. 2. a). In parallel with these efficiency gains, global module prices collapsed by roughly one order of magnitude over the last two decades, from around 6–7 $/W in the early 2000s to about 0.26 $/W by 2024, a decline on the order of 90–95 %, which underpins the rapid commercialization of PV at terawatt scale (Fig. 2. b).

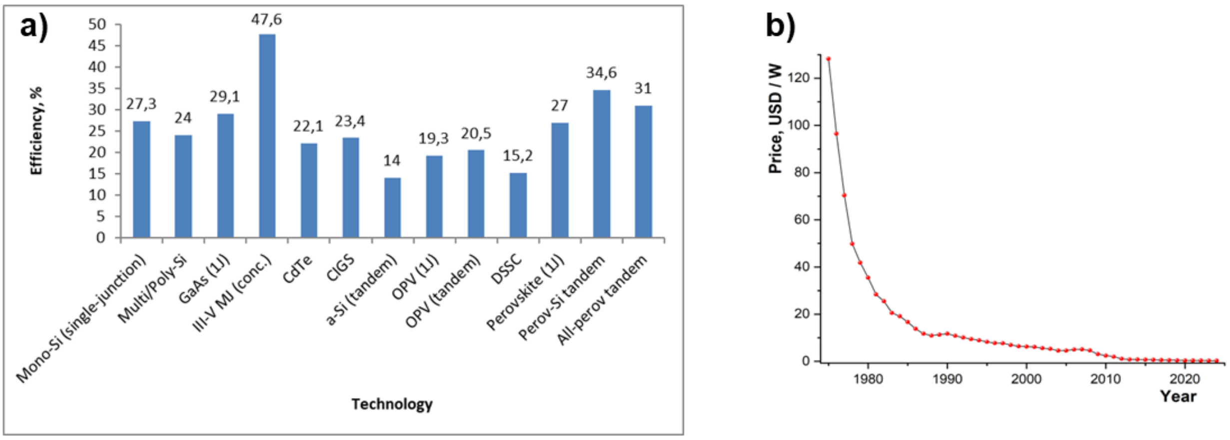

Figure 2. Record efficiencies of key photovoltaic technologies (a); Inflation-adjusted PV module prices, 1975–2025 (b) (Author's source).

At the same time, record efficiencies must be clearly distinguished from technologies that form the practical backbone of global PV deployment. Crystalline silicon modules provide the overwhelming majority of installed capacity. CdTe contributes significantly in utility scale thin film installations. CIGS, amorphous silicon, organic and dye sensitized technologies remain specialized. III-V and complex multi junction stacks are essential in space power and high concentration systems, but their material and cost profiles are incompatible with mass terrestrial deployment. Perovskite and perovskite silicon tandem modules are emerging at pilot scale and could become a major component if stability and reliability targets are met.

Historically successful PV technologies share not only high conversion efficiencies, but also the use of elements with secure and scalable supply, compatibility with large area industrial processing, proven durability over decades in outdoor conditions, and favorable levelized cost of electricity under realistic spectra and climates.

Systems that depend on scarce or toxic elements, fragile liquid components, intricate multi element stoichiometry, or unresolved degradation mechanisms tend to remain confined to niches despite impressive laboratory records.

In this sense, the history of sunlight to electricity conversion provides a reference template for the rest of this review. It demonstrates that absorber electronic structure, junction and interface design, and spectral management must be evaluated together with resource availability, stability, manufacturing routes, and end of life strategies. These same constraints will recur in the analysis of solar fuels, photocatalytic remediation, and light charged storage technologies in the following sections.

3. Sunlight to Chemical Bonds: Solar Fuels, PEC, and CO_2 Reduction.

Converting sunlight into storable chemical energy proceeds through three tightly linked routes: photoelectrochemical water splitting in liquid junctions, particulate photocatalysis in suspensions or sheets, and photovoltaic-powered electrolysis that couples solid-state PV with commercial electrolyzers. Performance is measured as solar-to-hydrogen or, more generally, solar-to-chemical efficiency, defined by the

Gibbs free energy stored per incident solar power under AM 1.5 G illumination with a specified device geometry and product accounting. Meaningful comparison also requires long-term stability under operating current, corrosion resistance at the semiconductor-electrolyte interface, and reliance on scalable, low-toxicity materials (Walter, Warren, McKone, Boettcher, Mi, Santori, & Lewis, 2010).

3.1. Photoelectrochemical Water Splitting.

Modern PEC begins with the 1972 report of bias-assisted water splitting on TiO_2, which established the semiconductor-electrolyte junction as a workable solar-fuel architecture (Fujishima & Honda, 1972).

An integrated path to the required photovoltage arrived in 1998 with a $GaInP_2$/GaAs tandem that split water at 12.4 % solar-to-hydrogen in a monolithic photovoltaic-photoelectrochemical device, setting the benchmark for unbiased operation and certified reporting (Khaselev & Turner, 1998). Subsequent progress centered on protection layers and catalysts that pass carriers while blocking corrosion. Conformal amorphous TiO_2 grown by atomic layer deposition became a widely adopted strategy, stabilizing Si, GaAs, and GaP photoanodes during oxygen evolution without sacrificing electronic contact (Hu, Shaner, Beardslee, Lichterman, Brunschwig, & Lewis, 2014). With careful interface and catalyst engineering, perovskite absorbers have now been integrated into fully submersed PEC cells that reach 20.8 % solar-to-hydrogen, demonstrating that high photovoltage and defect tolerance can coexist in aqueous operation (Fehr et al., 2023).

3.2. Particulate Photocatalysis.

A complementary route disperses light absorbers as powders or immobilized sheets and collects product gases directly from the reactor. Recent demonstrations report 9.2 % solar-to-hydrogen using InGaN-based catalysts under concentrated sunlight and pure water, while outdoor panels have validated scale-up concepts and highlighted the central challenges of bubble management, mass transport, and long-term catalyst integrity (Zhou et al., 2023). These results show that high optical cross-sections and cocatalyst engineering can deliver competitive efficiency, while practical deployment hinges on stable reactor designs and efficient gas separation.

3.3. PV–Electrolysis Coupling.

Using mature photovoltaics to drive state-of-the-art electrolyzers currently sets the commercial baseline and the near-term efficiency ceiling. Laboratory one-sun systems that electrically match multijunction PV to low-overpotential electrodes have exceeded 30 % solar-to-hydrogen, with a straightforward durability pathway that leverages existing PV and electrolyzer supply chains (Jia et al., 2016).

3.4. CO_2 Reduction: From Proofs to Selective and Integrated Systems.

Photoassisted CO_2 conversion was demonstrated soon after PEC water splitting. In 1978, p-GaP photocathodes reduced aqueous CO_2 to C_1 products under illumination in liquid-junction cells, followed in 1979 by illuminated semiconductor suspensions that produced formate, formaldehyde, methanol, and methane, thereby establishing both photoelectrochemical and particulate routes (Halmann, 1978; Inoue, Fujishima, Konishi, & Honda, 1979). Homogeneous molecular catalysis delivered early selectivity milestones, notably with $Re(bpy)(CO)_3X$ complexes that reduce CO_2 to CO under visible light and inspired extensive mechanistic and ligand-design work, including Mn analogues based on earth-abundant metals (Johnson, George, Hartl, & Turner, 1996). On heterogeneous electrodes, copper remains unique in forming multi-carbon products, while gas-diffusion architectures and electrolyte design have lifted currents and selectivity; comprehensive reviews codify activity-selectivity trends and the remaining scale-up barriers (Nitopi et al., 2019). Fully solar-integrated devices have progressed from perovskite-powered CO_2-to-CO leaves at more than 6.5 % solar-to-CO to flow electrolyzers coupled to triple-junction PV that approach about 20 % solar-to-CO at high Faradaic efficiency, illustrating that selective CO production is technically within reach, while multi-carbon liquids still require advances in catalyst stability and carbon-capture integration (Gao et al., 2022; Schreier et al., 2015).

3.5. Nitrogen Fixation Under Sunlight.

Solar ammonia is an appealing target because ammonia is both a fertilizer and a potential energy carrier, yet direct nitrogen reduction remains technically and metrologically challenging. Recent reviews compare photocatalytic, photoelectrochemical, PV-electrocatalytic, and photothermal approaches, emphasize the extreme inertness of N_2, and call for careful benchmarking of solar-to-ammonia figures of merit and productivity per illuminated area (Collado, Pizarro, Barawi, García-Tecedor, Liras, & de la Peña O'Shea, 2024). The field has been shaped by rigorous protocols that use $^{15}N_2$ labeling and contamination control to avoid false positives from ambient ammonia or nitrogen-containing impurities. These studies show that many early reports overestimated activity and that validated rates at ambient conditions are still very low, although lithium-mediated and tandem-catalyst concepts provide credible mechanistic pathways for progress (Andersen et al., 2019; Choi et al., 2020). In parallel, nitrate and nitrite reduction offer near-term solar routes to ammonia that are relevant for wastewater valorization, while true N_2-to-NH_3 photofixation will require stable catalysts with demonstrable turnover, standardized ^{15}N accounting, and device architectures that combine selective cathodes with robust photoanodes.

3.6. Status and Outlook.

Among solar-fuel strategies, PV-electrolysis is already commercial and benefits directly from PV and electrolyzer learning curves, while particulate photocatalysis and integrated PEC are pre-commercial despite rapid efficiency gains and credible outdoor scale-ups (Jia et al., 2016). For CO_2 reduction, selective CO and formate production has reached device-level solar-to-chemical figures above ten percent in some architectures, whereas durable solar routes to multi-carbon liquids remain research-stage and hinge on suppressing degradation at reactive interfaces and on efficient carbon capture coupling (Gao et al., 2022; Nitopi et al., 2019). For nitrogen, the consensus from best-practice studies is that validated solar ammonia rates are presently far from practical targets, which makes nitrate and nitrite upgrading attractive interim objectives while mechanistically guided catalyst design and standardized ^{15}N protocols continue to advance the true N_2 pathway (Andersen et al., 2019; Choi et al., 2020). Across all routes, the shared materials playbook is clear: align band edges with target redox reactions, control defects and buried interfaces to suppress recombination and corrosion, engineer catalytic microenvironments for selectivity, and favor abundant elements and scalable processing from the outset (Walter, Warren, McKone, Boettcher, Mi, Santori, & Lewis, 2010).

4. Sunlight to Environmental Remediation: Photocatalysis for a Cleaner Planet.

Environmental photocatalysis uses illuminated semiconductors to oxidize or transform pollutants in water and air and to maintain self-cleaning or antimicrobial surfaces. Performance is commonly reported as apparent quantum yield, pseudo first order rate constants normalized to surface area or catalyst mass, and for air depollution as areal removal rates of NO and NO_2 under standard gas flows and illumination. Robust benchmarking requires explicit photon accounting, control of mass transfer, and durability testing under realistic humidity, temperature, and fouling conditions, together with careful identification of intermediates and mineralization products (Hoffmann, Martin, Choi, & Bahnemann, 1995; Nakata & Fujishima, 2012).

4.1. Foundational Demonstrations and the TiO_2 Benchmark.

Early heterogeneous studies showed that illuminated semiconductor powders can oxidize toxic anions and organics, which positioned TiO_2 as the reference material for environmental remediation and mechanistic work on radical-driven pathways and interfacial charge transfer (Frank & Bard, 1977; Hoffmann, Martin, Choi, & Bahnemann, 1995). The concept of transparent self-cleaning TiO_2 coatings on glass was then introduced, establishing a route to photodegrade organic films directly on surfaces and to couple photocatalysis with photoinduced hydrophilicity that enables rain assisted cleaning in real environments (Paz, Luo, Rabenberg, & Heller, 1995; Paz & Heller, 1997).

4.2. Extending Activity Into the Visible.

Classic TiO_2 responds mainly to UV-light. Band gap engineering and dopants were adopted to harvest a larger fraction of sunlight. A landmark was the report of visible light activity in nitrogen doped TiO_2, which stimulated extensive work on anion and cation modified oxides and on defect mediated absorption tails (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001). In parallel, metal free graphitic carbon nitride emerged as a visible light photocatalyst and broadened the palette of materials used in environmental and solar fuel transformations, often in heterojunctions with oxides to improve charge separation and spectral coverage (Nakata & Fujishima, 2012; Xinchen Wang et al., 2009).

4.3. Water Treatment: Organics, Dyes, and Pharmaceuticals.

In water, semiconductor photocatalysts target dyes, endocrine disruptors, antibiotics, and other micropollutants. Reviews have consolidated kinetics, reactor geometries, and pathways, including the roles of hydroxyl radicals, valence band holes, and adsorbed oxygen species, and have emphasized that real matrices with natural organic matter and carbonate buffers can suppress apparent rates relative to idealized lab solutions (Chong, Jin, Chow, & Saint, 2010). Immobilized films and photocatalytic membranes reduce post treatment separation steps but introduce additional mass transfer limitations that must be accounted for in reporting.

4.4. Air Depollution and Building Materials.

Gas phase depollution focuses on NO and NO_2 abatement, volatile organic compounds, and bioaerosol inactivation. Laboratory assessments for NO_x commonly adopt the ISO 22197 methodology, and large bodies of work have translated oxide photocatalysts into cements, renders, and coatings for building and urban infrastructure. Field deployments and meta-analyses report both promising reductions and significant variability depending on irradiance, humidity, pollutant load, and substrate weathering, which underscores the need for realistic illumination and flow conditions, as well as for long term durability studies and maintenance protocols (Dahl, Jensen, Bigi, & Ghermandi, 2023; Russell, Frederickson, Hertel, Ellermann, & Jensen, 2021; Sanchez, Santiago, Martilli, Palacios, Núñez, Pujadas, & Fernández-Pampillón, 2021).

4.5. Architectures and Interfacial Design.

Modern environmental photocatalysts rarely rely on a single oxide in isolation. Heterojunctions with type II, direct Z-scheme, or S-scheme band alignments and plasmonic or carbonaceous co components are designed to improve charge separation and reaction selectivity, while cocatalysts such as Pt, Pd, or transition metal oxides accelerate specific interfacial steps. The most durable coatings balance optical absorption with porosity and wettability, incorporate binders and UV stabilizers compatible with outdoor exposure, and maintain activity after soiling and cleaning cycles. These strategies follow the same playbook as solar fuel photocatalysis, adapted to low reactant concentrations and to mass transfer regimes dominant in thin films and porous surfaces (Hoffmann, Martin, Choi, & Bahnemann, 1995).

Environmental photocatalysis is technologically mature for niche but impactful uses, including self-cleaning glazing, anti-fogging and antimicrobial surfaces, and specialty cements for localized NO_x abatement. At city scale, measured impacts vary widely and depend on climate, geometry, and maintenance, so rigorous outdoor trials with standardized reporting remain essential before broad municipal deployment claims can be generalized (Sanchez, Santiago, Martilli, Palacios, Núñez, Pujadas, &

Fernández-Pampillón, 2021). Continued progress will come from realistic reactor engineering, better photon management in scattering media, catalysts that maintain activity under complex environmental exposures, and life cycle assessments that include end of life handling of photocatalytic surfaces. As with other sunlight driven technologies, success depends on aligning band structures and interfaces with the target chemistry, sustaining activity under real operating stressors, and choosing abundant, low toxicity elements that can be manufactured and maintained at scale (Hoffmann, Martin, Choi, & Bahnemann, 1995).

5. Emerging Light-Charged Devices: From Photo-Batteries to Molecular Photochemical Cells.

Devices that harvest light and store the harvested energy inside the same architecture now span several families. Photocapacitors couple a photovoltaic or sensitized junction to an electric-double-layer or pseudocapacitive reservoir inside one stack. Photo-batteries integrate light absorbers with intercalation hosts so that illumination directly charges a redox pair. Solar flow batteries merge light harvesting with dissolved redox couples that can be circulated and stored. A newer molecular branch uses light to shift chemical equilibria and thereby build ionic gradients that are then converted to electrical work. Across all of these, the central figures of merit are solar-to-stored or solar-to-output efficiency, charge and energy per unit area, retention in the dark, cycling durability, and scalability of the materials set.

5.1. Historical Stepping Stones and Archetypes.

Early dye-sensitized photocapacitors proved that a single, compact stack can both generate and store charge. A two-electrode dye-sensitized “photocapacitor” was introduced in 2004, followed by a three-electrode configuration in 2005 that raised the charge-state voltage and areal energy density by engineering separate photo- and storage electrodes within one device (Miyasaka & Murakami, 2004; Murakami, Kawashima, & Miyasaka, 2005). A comprehensive modern synthesis of the photocapacitor field is provided by a 2023 Chemical Reviews article that maps device layouts, materials choices, and loss channels (Flores-Diaz, De Rossi, Das, Deepa, Brunetti, & Freitag, 2023).

5.2. Photo-Batteries and Photo-Assisted Batteries.

Photo-batteries aim to directly raise the electrochemical potential of an insertion compound under illumination, so that charging proceeds without an external photovoltaic panel. Two-electrode demonstrations include light-assisted delithiation of $LiFePO_4$ hybrid photocathodes, which established clear photo-driven shifts in state of charge and offered a mechanistic template for band-edge alignment to battery redox couples (Paolella et al., 2017). More recently, architectures that exploit semiconductor-insertion heterojunctions have delivered fully photo-rechargeable Li-ion operation under ambient light with vanadium oxide based cathodes and related designs, while also clarifying how to separate true photocharging from thermal artifacts (Liu et al., 2024; Pujari, Kim, Abbasi, Lee, Greenham, & De Volder, 2024; Salunke, Chamola, Mathieson, Boruah, de Volder, & Ahmad, 2022). These studies converge on practical conditions for light-rechargeability: the quasi-Fermi level under illumination must exceed the intercalation or plating potential at the negative electrode, interfaces must pass charge faster than recombination, and the device must be optically and ionically balanced to avoid parasitic losses.

5.3. Solar Flow Batteries.

Solar flow batteries integrate a photoelectrode or photovoltaic junction with a redox-flow cell so that light input is converted and parked in liquid redox couples. Monolithic laboratory devices have reached double-digit solar-to-output electricity efficiency, including a III-V based integrated cell at 14.1 % and a single-junction GaAs photoelectrode based system at 15.4 %, while subsequent work has mapped design rules for photoelectrodes, redox pairs, and light management in integrated stacks (Bae, Kanellos, Faasse, Dražević, Venugopal, & Smith, 2020; Cao, Skyllas-Kazacos, & Wang, 2018; Fu, Li, Yang, Lin, Veyssal, He, & Jin, 2021; Li, Fu, Zhao, He, & Jin, 2018; Lu, Leung, Su, Yang, & Xu, 2021). The attraction of the flow format is the decoupling of power and energy through external electrolyte tanks, together with the use of mild redox kinetics that relax stability demands on the illuminated components (Fu, Li, Yang, Lin, Veyssal, He, & Jin, 2021).

5.4. A Spiropyran-Based Light-Rechargeable Concentration Cell.

A recent molecular blueprint replaces the semiconductor junction with a photoswitchable coordination complex whose light-driven chemistry generates the charging force. The device uses identical zinc electrodes separated by a membrane and filled with a solution of a Zn-spiropyran complex in acetonitrile. When one half-cell is illuminated with visible light, the complex partially decoordinates and releases free Zn^{2+}, which creates a concentration gradient between the bright and dark sides. The gradient sets a Nernst-type electromotive force that is read out between the two zinc electrodes. In the dark, the complex reforms and the system resets, enabling repeated, autonomous light-induced recharge cycles with reproducible tens of millivolts per cell and microampere-level currents, including operation with a smartphone LED (Hrebonkin & Bulavko, 2025). The choice of zinc addresses availability and toxicity, while the aprotic solvent supports reversible complexation and free-ion populations. The key novelty is the direct conversion of photon-controlled coordination equilibria into ionic chemical potential, with no semiconductor junction and no external bias, which establishes a distinct class of “molecular photochemical cells” governed by equilibrium thermodynamics rather than photovoltage at a solid-liquid interface (Figure 3) (Hrebonkin & Bulavko, 2025).

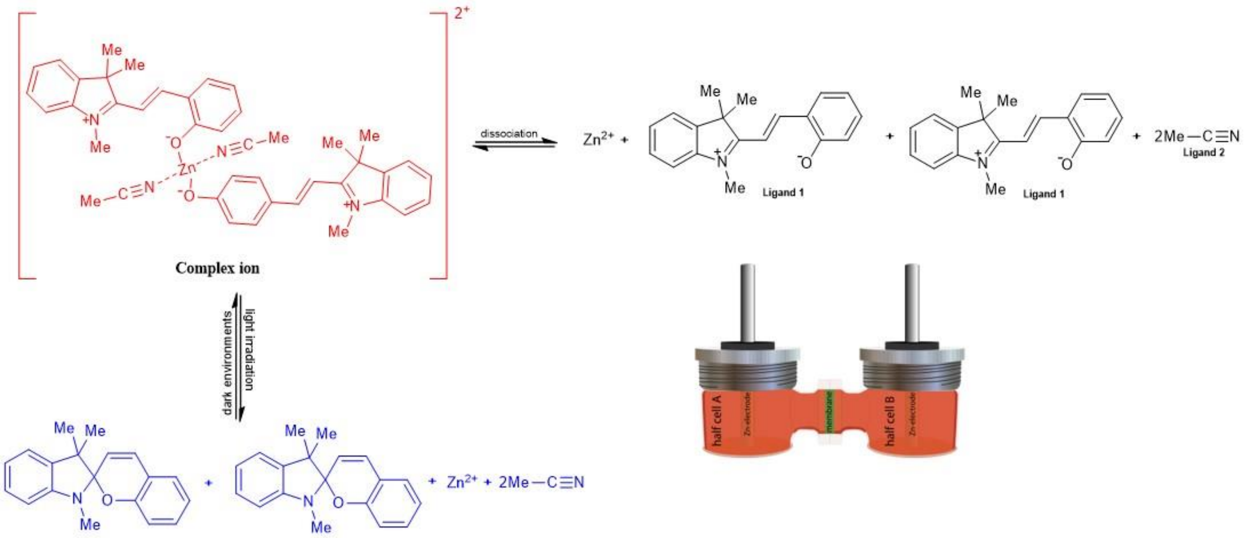

Figure 3. Spiropyran-based photoelectrochemical cell with light-induced charging: schematic of the Zn-spiropyran complex and a symmetric Zn–Zn H-cell (Hrebonkin & Bulavko, 2025).

The spiropyran cell decouples light harvesting from solid-state junctions and shifts the optimization space to photochemical equilibrium contrast, diffusion control, and membrane selectivity. Photovoltage scales with the logarithm of the Zn^{2+} activity ratio, so higher contrast requires complexes that exhibit large, reversible light-induced shifts in stability constants, faster forward photokinetics relative to back reactions, and separators that suppress back-diffusion without excessive ohmic loss. Concentrating the photoactive volume near the separator, patterning bright and dark regions at short distances, raising complex concentration within solubility limits, and tethering spiropyrans to polymer backbones to reduce crossover are clear materials levers. The same principle is extendable to alternative ligands, counter-anions, and even aqueous media if reversible coordination can be retained in water.

Relative to photocapacitors, storage here resides in a solution-phase chemical potential gradient rather than in electron-ion layers at internal interfaces. Unlike photo-batteries, no intercalation hosts are required, so mechanical strain and the formation of new solid interfaces are avoided. In contrast to solar flow batteries that rely on photovoltage-generating photoelectrodes and often precious-metal catalysts, this device uses a photoswitchable complex that can, in principle, be formulated from abundant elements. The present trade-offs are modest per-cell voltage and diffusion-limited current, both of which can be mitigated by cell geometry, ion-selective membranes, and series stacking.

5.5. Materials Playbook and Metrics.

For all light-charged platforms, the core constraints rhyme. Band-edge alignment to battery redox couples determines whether light can do useful charging work in photo-batteries, and this has been formalized in recent analyses that provide practical diagnostics for true photocharging versus photothermal effects (Pujari, Kim, Abbasi, Lee, Greenham, & De Volder, 2024). In photocapacitors, optical coupling between the light absorber and the storage element, interfacial series resistance, and electrolyte stability set the ceiling for areal energy and round-trip efficiency (Flores-Diaz, De Rossi, Das, Deepa, Brunetti, & Freitag, 2023). In solar flow batteries, the pairing of photoelectrode output with redox couple potentials, light management at the semiconductor-electrolyte interface, and crossover suppression dictate the achievable solar-to-output electricity efficiency and the service lifetime (Bae, Kanellos, Faasse, Dražević, Venugopal, & Smith, 2020; Li, Fu, Zhao, He, & Jin, 2018).

5.6. Use cases and Near-Term Prospects.

Photocapacitors and compact photo-batteries are natural candidates for self-powered sensors, badges, and micro-actuators where transparency, low weight, and minimal part count are prized over absolute areal power. Solar flow batteries bridge toward distributed and grid-adjacent storage by separating light harvesting from storage volume and enabling safe, long-life electrolytes. Molecular photochemical cells, inaugurated by the spiropyran concentration-cell concept, target low-voltage light-rechargeable sources that can be addressed optically and fabricated from commodity components, with a clear route to series stacking and arrayed operation for higher voltages (Hrebonkin & Bulavko, 2025).

5.7. Outlook.

The field is diversifying beyond semiconductor-centric stacks. Photocapacitors and photo-batteries will continue to push energy densities through better heterojunction design and transport management, guided by emerging quantitative criteria for light-rechargeability and by strategies that suppress photodegradation at buried interfaces (Flores-Diaz, De Rossi, Das, Deepa, Brunetti, & Freitag, 2023; Pujari, Kim, Abbasi, Lee, Greenham, & De Volder, 2024). Solar flow batteries will likely define the high-efficiency end of integrated conversion-plus-storage for liquid redox systems, with demonstrated double-digit solar-to-output efficiencies and credible stability pathways (Fu, Li, Yang, Lin, Veyssal, He, & Jin, 2021; Li, Fu, Zhao, He, & Jin, 2018). The spiropyran platform offers a complementary molecular route: illumination writes a chemical-potential gradient that is read electrically and erased in the dark. This opens a wide search space for robust, photoresponsive complexes and improved separators. Immediate priorities are to increase per cell voltage, quantify the full cycle efficiency from solar input to stored energy and then to delivered electricity, demonstrate stability over many cycles, and shift operation to benign solvents, including water. On the strength of the first reproducible visible light self-recharging cell and a clear set of controllable parameters, this concept credibly expands the design space for light charged electrochemical systems (Hrebonkin & Bulavko, 2025).

6. Discussion.

The four sunlight-driven pathways examined above developed largely within separate research communities, yet their historical trajectories reveal a set of shared patterns that merit explicit comparison. In each domain, the initial proof of concept relied on a wide-band-gap oxide or a high-purity crystalline semiconductor, and subsequent progress depended on expanding the spectral response, improving interfacial charge transfer, and reducing reliance on scarce or toxic constituents. The order in which these challenges were addressed, and the degree to which they have been resolved, differs substantially across the four fields, and these differences explain much of the variation in technological maturity observed today.

Photovoltaics have advanced furthest along the path from laboratory discovery to industrial scale. The decisive factors were not peak efficiency alone but the convergence of adequate performance with processability, durability, and cost reduction over decades of incremental engineering. Crystalline silicon exemplifies this pattern most clearly. By contrast, solar fuels and photoelectrochemical systems, despite reaching impressive solar-to-chemical efficiencies in controlled settings, have not yet resolved the corrosion, sealing, and catalyst stability issues that limit continuous outdoor operation. The gap between photovoltaic and solar-fuel maturity is therefore less a matter of fundamental physics than of materials durability and systems engineering under realistic conditions.

Environmental photocatalysis occupies an intermediate position. Self-cleaning coatings and depolluting cements have reached commercial deployment, but their performance in the field varies widely depending on irradiance, humidity, and surface fouling. The recurring lesson is that laboratory photocatalytic rates measured under idealized illumination and gas flow often overestimate real-world outcomes, a problem that closely parallels the overestimation of solar-fuel yields in early reports that lacked rigorous product quantification.

Light-charged storage devices remain the least mature of the four classes, yet they illustrate an important convergence: the same band-edge alignment, interfacial passivation, and charge-transport criteria that govern photovoltaic and photoelectrochemical performance also determine whether a photo-battery or a solar flow battery can deliver useful charging work. The recent emergence of molecular photochemical cells, which replace semiconductor junctions with photoswitchable coordination equilibria, suggests that the design space for coupling light absorption to energy storage is broader than early device concepts implied.

Across all four domains, a consistent hierarchy of constraints governs whether a given materials platform progresses beyond the prototype stage. Efficiency is necessary but not sufficient; long-term operational stability under realistic environmental stresses acts as the primary filter. Beyond stability, the availability and toxicity of constituent elements, compatibility with scalable manufacturing, and prospects for end-of-life recovery determine whether a technology can be deployed at the scale required for meaningful impact on the energy system. Technologies that address these constraints from the outset tend to advance faster and more reliably than those that defer them to later development stages.

The comparison also highlights a productive feedback loop among the four pathways. Protection layers developed for photoelectrochemical anodes have informed encapsulation strategies for perovskite solar cells. Heterojunction concepts optimized for photocatalytic charge separation have been adapted for photo-battery cathodes. Photon management techniques refined in tandem photovoltaics are now applied to particulate photocatalyst sheets. Recognizing these cross-pathway transfers as a deliberate design strategy, rather than as incidental borrowing, can accelerate materials development in each field by drawing systematically on solutions already validated in adjacent domains.

7. Conclusions.

Across all sunlight-driven technologies a consistent tradeoff governs progress. Simple and scalable chemistries tend to defeat exotic but fragile ones. Crystalline silicon, robust oxides, and durable polymer or glass matrices moved from lab curiosity to industry because they tolerate imperfect processing and outdoor stress and because they fit established manufacturing lines. Systems that depend on rare elements, tight stoichiometry windows, or many tightly coupled layers often stall at the prototype stage. Record efficiency matters only when it travels together with bankability, predictable yield, and a supply chain that can grow to the terawatt scale.

The history of photovoltaics illustrates this rule. Silicon did not become dominant by peak numbers alone. It combined respectable efficiency with multi-decade stability and a learning curve that collapsed cost. Thin-film CdTe and CIGS earned durable niches by balancing absorber quality with throughput and recycling plans. By comparison, DSSC and most organic PV architectures delivered elegant physics and attractive form factors yet struggled outdoors over long lifetimes. Perovskites are the present test case. They already rival the best single-junction silicon cells and they unlock practical tandems, yet long-term stability, ion migration, and encapsulation still set the pace for deployment. The same pattern repeats in solar fuels and environmental photocatalysis, where stable interfaces, corrosion control, and benign electrolytes are decisive. High solar-to-chemical figures are not enough without operation over many hundreds or thousands of hours under realistic illumination, temperature, and mass-transfer conditions.

Materials choices are also filtered by toxicity, critical-element exposure, and prospects for circularity. Silicon scores well on abundance and end-of-life recovery. CdTe and CIGS show that elements with toxicity or supply constraints can still be viable when processes are tightly contained and recycling is proven. For PEC and flow systems, precious metals are acceptable only in trace amounts and only when protected against loss. Emerging light-charged devices should begin with benign solvents and abundant ions, then add performance. Designing for disassembly, solvent recovery, and closed-loop electrolyte management should be a baseline requirement rather than a late addition.

The four technology tracks connect into one sunlight infrastructure. Photovoltaics are the backbone that already powers commercial electrolyzers for hydrogen and can drive electrochemical CO_2 conversion where catalysts are selective and durable. PEC and particulate photocatalysis offer compact, direct solar-to-fuel routes where wiring and power electronics are impractical and they serve as testbeds for protection layers and catalysts that can later migrate into PV-coupled plants. Environmental photocatalysis sits at the hygiene and maintenance layer of the same system. Self-cleaning and depolluting surfaces preserve optical throughput, extend service intervals, and reduce chemical use in buildings and water systems. All tracks share the same engineering vocabulary: band-edge alignment, defect and interface passivation, photon management in scattering media, and credible life-cycle accounting.

Where progress proved durable, the winning strategies favored defect tolerance, simple stacks, and forgiving processes. Textured silicon with high-quality passivation, single-phase oxides with robust cocatalysts, and flow batteries with mild electrolytes all fit this pattern. Where progress stalled, warning signs were visible early. Liquid electrolytes in large outdoor devices without guaranteed sealing, unstable redox shuttles, photofixation claims without isotope validation, and stacks that multiply optical interfaces and buried boundaries tend to fail in scale-up. In CO_2 and nitrogen conversion, rigorous metrology became the gatekeeper. Gas-diffusion architectures, isotopic labeling, and quantitative product analysis filtered optimistic reports and clarified which routes are ready for coupling to sunlight at useful rates.

Near-term opportunities are pragmatic and specific. Perovskite-silicon tandems are the most immediate step beyond the single-junction limit, provided ion migration and interfacial degradation are suppressed with stable transport layers and strong encapsulation. Integrated PEC platforms can matter where direct solar fuels make sense, especially if protection layers and earth-abundant catalysts deliver thousands of hours in buffered electrolytes. Solar flow batteries already show double-digit solar-to-electricity output with credible lifetimes and offer a modular way to combine light capture with storage volume. In environmental photocatalysis, durable heterojunction coatings, standardized outdoor testing, and designs that keep activity through soiling and cleaning cycles will separate deployable products from laboratory curiosities.

Within light-charged storage, a complementary molecular branch has appeared. The spiropyran-based concentration cell demonstrates that illumination can write a chemical-potential gradient in solution that is read electrically and erased in the dark. This route stores solar input without solid intercalation hosts or heavy photoelectrodes and uses abundant elements. First devices deliver modest voltage and diffusion-limited current, yet they offer clear levers for improvement: stronger light-driven equilibrium shifts, shorter diffusion paths, ion-selective membranes, and series stacking. The broader idea is to exploit reversible light-controlled coordination or acid-base equilibria to create simple, transparent charge reservoirs. Such cells are unlikely to compete with PV for bulk power, but they can fill low-voltage niches, seed new hybrid chemistries, and add design freedom to photocharged electrochemistry.

These considerations motivate a set of system level recommendations for the decade ahead. Focus on interfaces first, because buried contacts and transport layers set both stability and efficiency whether the target is a tandem PV, a PEC-stack, a photocatalytic wall, or a light-charged cell. Use standardized, device-relevant metrics: AM 1.5 G power accounting for PV and PEC, photon-to-product balances for photocatalysis, round-trip efficiency and self-discharge for storage. Favor abundant elements and simple processes from the first prototypes so that scale-up paths are obvious. Build in recycling and recovery steps at design time, not after pilot runs. Couple materials discovery with realistic reactors and field trials so that durability and maintenance are measured rather than assumed.

Taken together, sunlight to electricity, to fuels, to clean air and water, and to stored charge are branches of the same design problem. The task is to place electronic levels and catalytic sites so that photons create carriers, carriers do useful chemistry, and the structure survives long enough to matter at scale. The record of the past half century is consistent. Technologies that align performance with stability, abundance, and manufacturability reshape the energy system; those that rely on fragile stacks, scarce elements, or optimistic metrology fade. The near-term landscape is therefore pragmatic. Silicon remains the base. Perovskite tandems, protected PEC cells, and solar flow batteries carry the next wave if durability and circularity are proven. Environmental photocatalysis improves the built environment where exposure and maintenance are matched to reality. Molecular light-charged cells open a fresh space for simple, optically addressed storage and sensing. Together these paths outline a realistic, connected, and scalable sunlight infrastructure.

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The author declare no conflict of interest.

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Сонячне світло на службі енергетики: Історична еволюція матеріалів для фотовольтаїки, сонячних палив, фотокаталізу та новітніх світлозаряджуваних пристроїв

Анотація. *У цьому огляді сонячне випромінювання розглядається як ключовий рушійний ресурс сталих технологій і аналізується, як розвивалися матеріали для захоплення, перетворення та зберігання сонячної енергії за окремими, але взаємопов'язаними функціональними шляхами. Історично обґрунтований і міждисциплінарний підхід застосовано до чотирьох основних* *класів процесів, керованих сонячним світлом: перетворення сонячного випромінювання на електроенергію, акумулювання сонячної енергії в хімічних зв'язках, фотокаталітична деградація забруднювачів та пряме світлоасистоване зберігання енергії. Еволюцію фотовольтаїчних систем розглянуто від кристалічного та полікристалічного кремнію до тонкоплівкових абсорберів, сенсибілізованих барвниками і органічних сонячних елементів, а також сучасних галогенідних перовськітів і тандемних конфігурацій, з акцентом на взаємозв'язок між ефективністю, стабільністю та доступністю матеріалів. Фотоелектрохімічні та каталітичні шляхи одержання сонячних палив проаналізовано з особливою увагою до розвитку оксидів металів, молекулярних комплексів, наноструктурованих каталізаторів і систем вибіркового відновлення* CO_2 *як платформ для зберігання сонячного світла в хімічних зв'язках. Фотокаталітичне усунення забруднень розглянуто в контексті проєктування напівпровідників, міжфазних процесів перенесення заряду та інтеграції світлозбиральних матеріалів у схеми очищення води й повітря. Останні досягнення у світлозаряджуваному та фотоасистованому зберіганні енергії, включно з фотобатареями, фотосуперконденсаторами, редокс-концепціями зберігання сонячної енергії та фоточутливими концентраційними комірками, оцінюються як нові підходи, спрямовані на поєднання поглинання фотонів, розділення заряду та його зберігання в єдиній архітектурі пристрою. У всіх цих доменах дослідження виокремлює повторювані принципи дизайну матеріалів, включно з оптимізацією ширини забороненої зони та вирівнювання зон, координаційного оточення каталізаторів, міжфазного й кінетичного контролю, експлуатаційної довговічності, опорою на поширені та малотоксичні елементи, а також сумісністю життєвого циклу з розгортанням у великому масштабі. Порівнюючи ці траєкторії в межах єдиної аналітичної рамки, робота окреслює спільні закономірності технологічних успіхів і невдач та визначає реалістичні напрями раціональної розробки адаптивних молекулярних, гібридних і напівпровідникових матеріалів для енергетичних та екологічних технологій наступного покоління, що працюють на основі сонячного випромінювання.*

***Ключові слова**: історія матеріалів; фотоасистоване накопичення енергії; світлозбиральні матеріали; відновлення* CO_2*; сталий дизайн матеріалів*

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