

Review

Mechanism and Air Cathode Materials of Photo-Assisted Zinc–Air Batteries for Photoelectrochemical Energy Storage

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Abstract

The photo-assisted strategy is an effective technology that combines both photo and electrical energy conversion/storage, which represents the direction of the next generation of green energy utilization technologies. In particular, photo-assisted zinc–air batteries (PAZABs) are novel and innovative devices with the advantages of high efficiency and environmental friendliness. Thanks to the generation and effective separation of photo-generated carriers in photo-response air cathode catalysts, PAZABs possess significantly accelerated kinetics of oxygen reduction reaction and oxygen evolution reaction. Moreover, as a popular kind of newly developed two-electrode photoelectrochemical energy storage device, which could realize direct solar-to-electrochemical energy storage, PAZABs alleviate the limitations of the intermittent nature of solar energy in practical applications. In this study, the working mechanism of photoelectrochemical energy storage devices and PAZABs are thoroughly and systematically introduced; additionally, the design principles and types of photo-response electrode materials are reviewed. Interface engineering has been proven to be an effective strategy to improve the performance of the photo-response air cathode catalysts in PAZABs. Thus, the crucial role of the modulated interface chemistry of heterostructure air cathode catalysts is also summarized. Subsequently, the recent progress in the development of single-atom catalysts is outlined. Finally, this review presents several potential strategies for overcoming bottlenecks in the practical application of PAZABs.



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Keywords: photoelectrochemical energy storage; photo-assisted zinc–air battery; heterostructure materials; interface effects; photoelectrochemical performances

1. Introduction

As a green secondary energy storage device, lithium-ion batteries (LIBs) have been successfully commercialized in various kinds of power supply equipment, including electric vehicles. However, the scarcity of lithium reserves in nature severely restricts the long-term and large-scale application of LIBs, while significantly increasing their costs [1,2]. Additionally, issues such as low energy density and significant safety hazards (thermal runaway, spontaneous combustion) seriously limit the further commercial development of lithium-ion batteries [1]. Consequently, developing new secondary energy storage systems to replace lithium-ion batteries has become an urgent societal need. Among various alternatives to lithium-ion batteries, zinc–air batteries (ZABs) have attracted significant attention from both the research and industrial communities due to their high energy density, enhanced safety, and low cost [2–4]. The performance of ZABs during charging and discharging is primarily determined by the oxygen reduction reaction (ORR) and

oxygen evolution reaction (OER) occurring at the air cathode. In practical ZAB applications, the electrochemical processes involve multi-electron reactions with multiple intermediate products. Unfortunately, the sluggish kinetics of these reactions severely hinder the rapid advance of this energy storage technology [5–7].

In ZABs, the primary commercial catalysts remain platinum group metals and their compounds (e.g., Pt/C, RuO₂, IrO₂). These commercial cathode catalysts are expensive and exhibit poor cycling stability, severely restricting the development of ZABs [8,9]. More significantly, the ORR and OER are based on entirely different reaction mechanisms and kinetics. However, noble metal catalysts cannot effectively catalyze both processes simultaneously. Therefore, developing high-performance, durable, and cost-effective multifunctional catalysts for use as air cathodes to enhance ZAB performance has become an urgent and challenging matter [10,11]. Recently, designing heterostructure catalysts with abundant interfaces has emerged as a research hotspot for achieving both ORR and OER catalysis while significantly improving reaction kinetics. In heterostructures, the direct contact between two components, owing to differences in their Fermi levels, geometric structures, and electron affinities, triggers unique interfacial properties (Figure 1), which are key to enhancing performance. Specifically, the following applies: 1. Charge Redistribution: Fermi level disparities induce built-in electric fields at the interface, leading to the redistribution of charge (electrons and holes), further suppressing the recombination of electron and hole. Separated carriers facilitate ORR and OER processes, improving reaction efficiency and kinetics [12,13]. 2. Lattice Strain: Mismatches in geometric structure and lattice constants generate compressive or tensile strain at the interface, causing d-band center shifts and defect formation [14,15]. 3. Chemical Bonding: Differences in electron affinity form interfacial chemical bonds, enabling electron transfer through these bonds [16]. These factors primarily enhance the catalytic activity of heterostructure bifunctional catalysts by modulating electronic structures. Additionally, reducing particle size to increase the exposed surface area can further enrich the number of active sites, thereby boosting catalytic performance.

In recent years, experimental techniques for minifying nanoparticle to single atoms, forming metal single-atom catalysts (SACs), have seen extensive development [17–19]. However, when the particle size is reduced to the single-atom scale, surface energy increases significantly, leading to severe aggregation. For the design of heterostructures, achieving the local confinement of single atoms is key to maximizing the exposure of active sites while preserving material structural integrity. To address this, substrate materials are introduced, and the metal–substrate interfacial interactions are utilized to anchor single-metal atoms, thereby overcoming aggregation and enabling the successful preparation of SACs. Additionally, to enhance metal–substrate interactions, coordination sites are often introduced into the substrate. Carbon-supported catalysts containing N-coordinated transition metals (M–N–C) are among the most widely studied SACs in ZABs [3,20–22]. In M–N–C catalysts, isolated atoms can coordinate with nitrogen in dual or quadruple configurations, forming stable metal–N₂/N₄–C moieties. The strong interactions in M–N–C ensure the stable anchoring of single atoms and robust catalyst structures, making the M–N–C catalysts ideal SACs. Among them, Fe- and Co-based SACs have attracted widespread research interest due to their outstanding performances [22–27]. Fe-/Co-based mono- [25,26], dual- [27], and tri-metal SACs can not only achieve bifunctional ORR/OER catalysis through the preparation of composite materials but also modulate the interfacial electronic structure by constructing single-atom catalytic sites, optimizing the adsorption energy of reaction intermediates, and simultaneously enhancing reaction kinetics, thereby advancing the development of high-performance zinc–air batteries (ZABs) for practical applications.

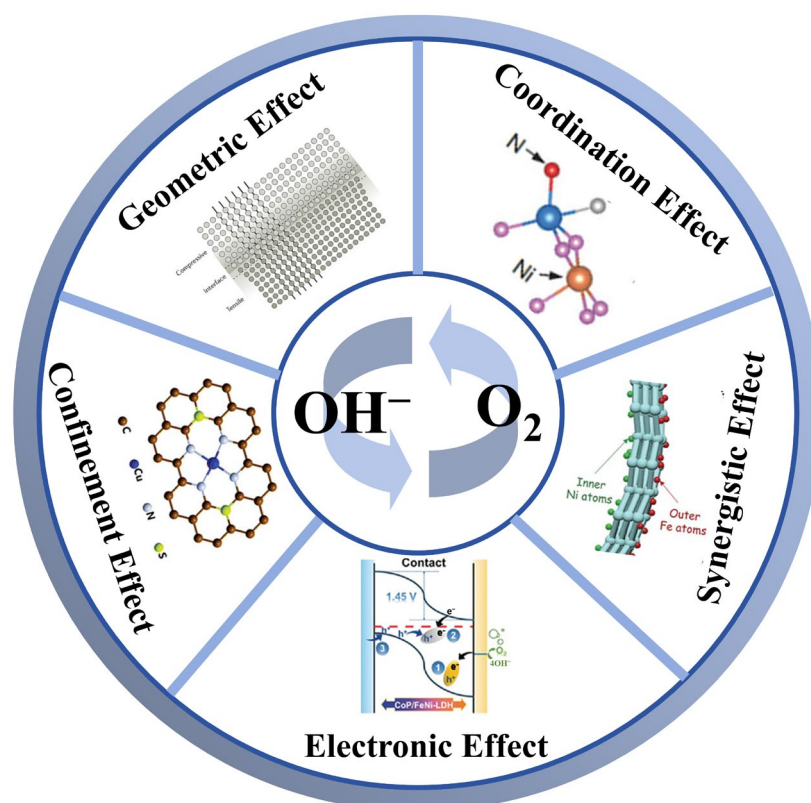


Figure 1. Interface effects for heterostructure catalysts.

However, in the reported studies, including those mentioned above, the impact of the photovoltaic effect on the catalytic performance of air cathodes in ZABs has seldom been investigated. When sunlight irradiates semiconductor materials, it excites photoelectrons, promoting electrons from the valence band to the conduction band and generating electron–hole pairs [28]. Leveraging the heterostructure, photo-generated electrons achieve more efficient separation (preventing electron–hole recombination), resulting in a further increase in charge density. Constructing photovoltaic-enhanced zinc–air batteries can integrate photochemistry and electrochemistry [13], while improving solar energy utilization and increasing the efficiency of ZABs. As early as 2017, Wang et al. [29] pioneered this approach by constructing a light-responsive $\text{Ni}_{12}\text{P}_5@\text{NCNT}$ bifunctional ORR/OER electrocatalyst. The p–n structure within the $\text{Ni}_{12}\text{P}_5@\text{NCNT}$ catalyst enabled enhanced ORR and OER electrocatalytic performance under light illumination due to its photovoltaic properties at the hetero-interface, leading to the fabrication of an integrated dual-electrode system for photoelectric conversion and electrochemical storage (Figure 2). Subsequently, the concept of integrated photoelectrochemical energy storage (PES) devices based on PES materials, enabling direct solar-to-electrochemical energy storage, has attracted a certain degree of attention in the scientific community [30,31]. Unlike photocatalytic/electrocatalytic systems (solar-to-chemical energy conversion) and photovoltaic systems (solar-to-electricity conversion), PES devices offer a direct pathway for solar energy storage as electrochemical energy [32–35].

Based on the emergence of photoelectrochemical energy storage (PES) devices and the research status of heterogeneous air cathode materials of ZABs, this review aims to summarize the following: (1) the features and operating principles of PES devices; (2) the material properties of heterojunction catalysts (including semiconductor–semiconductor and semiconductor–metal junctions); (3) the electrochemical performance of photo-assisted zinc–air batteries with heterojunction photocathodes. By analyzing the band structure,

optical properties, electrical properties and electrochemical performances of heterojunction catalysts, the underlying physical and chemical mechanisms at heterogeneous interfaces are elucidated. Ultimately, this work seeks to promote the development and utilization of solar energy by providing a reference for preparing high-efficiency zinc–air battery cells with photo-assisted units, dual-functionality cathodes, and fast reaction kinetics.

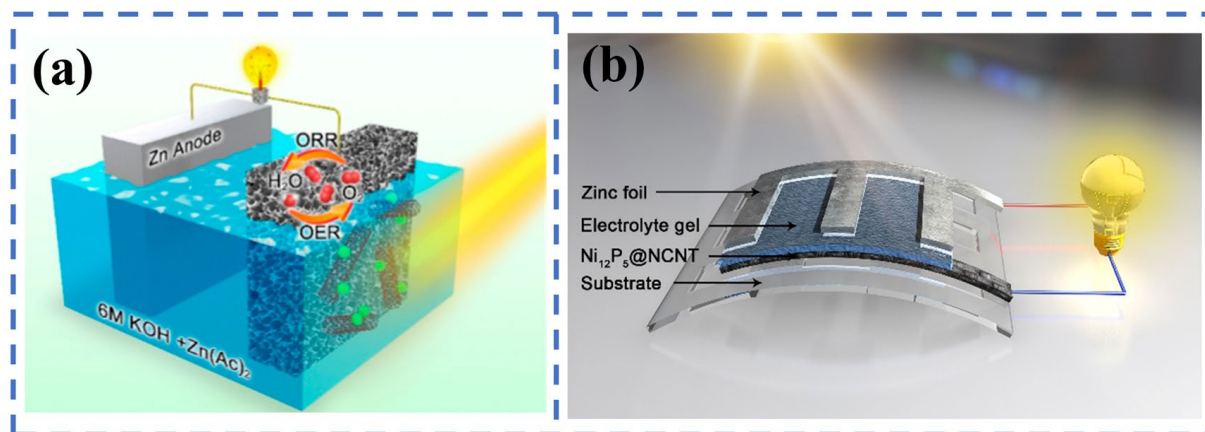


Figure 2. A two-electrode single device system with $\text{Ni}_{12}\text{P}_5\text{@NCNT}$ as photocathode and Zn as anode for efficient ORR and OER catalysis; bright yellow rays represent light illumination. Reproduced with permission [29].

2. Features of Photoelectrochemical Energy Storage (PES) Devices

The problems of environmental pollution and the depletion of fossil fuels have stimulated people's exploration of new green energy. Moreover, solar energy as an abundant and renewable energy resource has become the energy source with the greatest potential for satisfying the global energy demand by converting it into various types of energies. Generally, there are three types of current solar energy utilization technologies, including photovoltaics (PV), photo(electro)catalysis, and photoelectrochemical (PEC). Among them, PV devices based on perovskite materials have attracted great attention because they can directly output electrical energy for practical applications [36,37]. Meanwhile, the feature of photo(electro)catalysis technology is to convert solar energy into combustible fuels, such as CO , NH_3 , H_2 , etc. [38,39]. In addition, the photoelectrochemical (PEC) water-splitting technology, known as artificial photosynthesis, has the feature of being able to cyclically produce hydrogen.

2.1. General Concept and Principles of PES Devices

However, in order to achieve high stability applications under practical conditions, all the above technologies need to be combined with separate devices [40,41]. For example, PV devices need to be connected to electrochemical energy storage devices (lithium-ion batteries, supercapacitors, etc.) through wires (right part of Figure 3) to meet the electricity supply needs of people in daily life, which is the most traditional and common strategy for solar energy utilization. In addition, photo(electro)catalysis and photoelectrochemical (PEC) water-splitting technologies also need combination with separated regenerative fuel cells to achieve high-reliability utilization of solar energy (left part of Figure 3). These systems integrating two device units have several common drawbacks in practical applications. (1) Integrated systems are generally bulky, making them unable to meet the flexibility requirements of smart electronic products and electric vehicles [42]. (2) Commonly, there is a voltage or current mismatch between PV devices and energy storage batteries [43]. (3) There exists energy loss on the external wires, which reduces the energy utilization efficiency of

the whole system [43]. Considering this, the single device system with two electrodes has become a very attractive solution. In the single device system, a dual functional photoactive electrode is a main component, and then a photoelectrochemical energy storage cathode is connected with an anode to form a simple two-electrode configuration called a PES device (including PES ion batteries, PES Zn/Li metal–air batteries, PES supercapacitors, etc.) (middle part of Figure 3). The PES devices can directly store solar energy as electrochemical energy through a multifunctional PES cathode. The PES cathode material has the ability to convert and store energy, which determines the cost, stability, and solar-to-output energy storage efficiency of the two-electrode system (PES devices).

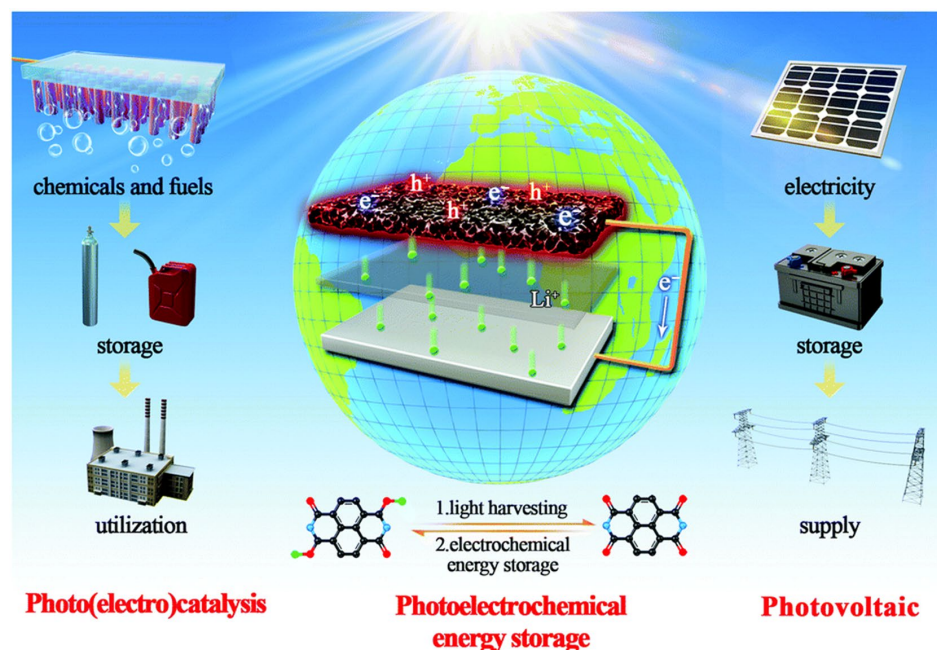


Figure 3. Schematic illustration of the features of the simple two-electrode configuration for direct solar energy storage into electrochemical energy, which are named photoelectrochemical energy storage (PES) devices; the bright rays at the top of the image represent sunlight. Reproduced with permission [30].

The solar-to-stored-energy conversion efficiency or the solar-to-electrochemical (STEC) efficiency is a key parameter for photoelectrochemical energy storage (PES) devices. Normally, the STEC efficiency (η_c) can be calculated using this formula: $\eta_c = E_{\text{output}}/E_{\text{light}} \times 100\%$, where E_{output} is the discharging energy from the device and E_{light} is the input light energy [30,44]. Typical PES devices, along with their STEC efficiencies and performances, are described in Table 1. Additionally, the specific STEC efficiency (η_c) of PAZABs can be calculated using the detailed formula: $\eta_c = E_A A_1 / P_{\text{in}} t A_2$, where E_A , A_1 , P_{in} , t , and A_2 represent areal energy density, catalyst surface area, light intensity, photocharging time and illuminated surface area, respectively [45]. In addition, the film thickness of active materials in photoelectrodes needs to match well with the diffusion length of photo-generated carriers. Only when the electrode material is thin enough can the diffusion path of charge carriers be shortened to meet the separation of short-lifetime carriers. However, the thin PES materials result in a low mass loading of active materials, which will reduce the energy storage capacity of the battery. Therefore, optimal film thickness/mass loading of active materials is crucial for fabricating high-performance PES devices. Normally, there is a “Loading-Diffusion Matching Formula”. This formula recommends that the film thickness $\leq$ carrier diffusion length $\times 1.2$. For example, the diffusion length of D-MoS₂ is 1.5 μm , so the corresponding film thickness should be $\leq 1.8 \mu\text{m}$,

which is approximately equivalent to an area loading of 4 mg/cm^2 [46–48]. Particularly, for wearable devices, the areal loading should be $\leq 4 \text{ mg/cm}^2$; the devices should be matched with elastic electrolytes (e.g., hydrogels with elongation at break $> 200\%$) to buffer bending stress; carbon cloth/carbon paper should be selected as the substrate to ensure the resistance change is $< 10\%$ after a large number (e.g., 1000 cycles) bending cycles [48–51].

Table 1. Typical PES devices, as well as their performances and the solar-to-electrochemical (STEC) efficiency (η_c).

Battery Type	PES Materials	Charge Potential Under Dark/Light	Capacity Under Dark/Light	Cycle Number	η_c	Ref.
LIB	TiO ₂	2.04/1.37	/	30	/	[52]
	N719 + LiFePO ₄	Photocharge	40/340 F g ^{−1}	115	0.06–0.08%	[53]
	V ₂ O ₅ /P3HT/rGO	Photocharge	118/161 F g ^{−1}	35	~0.22%	[54]
	NT-COF	2.53/2.02	129/200 F g ^{−1}	5	/	[55]
ZIB	V ₂ O ₅ /P3HT/rGO	Photocharge	190/370 F g ^{−1}	25	1.2%	[56]
	VO ₂ /rGO	Photocharge	282/315 F g ^{−1}	250	0.18%	[57]
	MoS ₂ /ZnO	Photocharge	245/340 F g ^{−1}	40	~0.2%	[58]
	g-C ₃ N ₄	3.61/1.96	/	70	/	[59]
LOB	ZnS@CNT	4.09/2.08	/	150	/	[60]
	TiO ₂ -Fe ₂ O ₃	4.2/3.2	/	100	/	[61]
	Siloxene nanosheets	3.80/1.90	--/1170 F g ^{−1}	100	/	[62]
	Co-TABQ	4.31/3.32	/	50	/	[63]
ZAB	a-Fe ₂ O ₃	1.97/1.43	598.7/--F g ^{−1}	50 h	/	[64]
	C ₄ N	~ 1.65/1.34	/	50	/	[65]
	PDTB and TiO ₂	1.88/0.59	/	~ 33	/	[66]
	Co ₃ O ₄	Photocharge	80.8/35.9 F cm ^{−3}	5000	/	[67]
SC	Ag@V ₂ O ₅	Photocharge	52/92 F g ^{−1}	4000	~0.05%	[56]
	g-C ₃ N ₄	1.00/0.68	6.65/11.4 F g ^{−1}	500	~0.01%	[68]
	ITO/P3HT	0.56/0.26	--/2.44 mF cm ^{−2}		~0.0017%	[69]
	Ti ₃ C ₂ T _x -NCDs	Photocharge	464/630 F g ^{−1}	900	/	[70]

2.2. PES Cathode Materials

To realize two-electrode PES devices, which directly store solar energy as electrochemical energy, dual functional photoactive electrodes as the main components play a very important role. In the system, dual functional photoactive materials generally go through two steps to store solar energy. Firstly, the air cathode needs to absorb solar energy and generate carriers (hole and electron pairs). Then, such charges take part in charge/discharge processes; thereby, transferring the energy to the electrochemical energy storage materials. The summary of the requirements for the PES materials is as follows: (1) The materials need to have appropriate bandgaps, with a range of 1.5–3 eV, which can ensure the effective capture of sunlight. (2) The effective separation of electron–hole pairs is crucial for further electrochemical energy storage. Based on this, PES materials must have the ability to separate positive and negative charges. (3) Extending the carrier lifetime and shortening the carrier diffusion distance are another principle of efficient PES material design. (4) PES materials must possess electrochemical energy storage properties. (5) The excited electron–hole pairs should be able to promote the process of electrochemical energy storage, or the excitation process should occur simultaneously with electrochemical energy storage. Therefore, the positions of the conduction band and valence band of the PES cathode need to be located within the potential window of redox of O₂. Many PES materials have been explored by researchers, among which heterostructures, combining photoelectric materials with energy storage materials, exhibit excellent multifunctional properties. Both inorganic and organic materials can be used as light capture agents or energy storage materials to form photoelectrochemical electrodes. The typical examples of using the heterojunctions as electrodes in PES devices will be discussed in the following section.

TiO₂ is a typical material that responds to ultraviolet light due to its wide bandgap characteristics. As a widely studied multifunctional material, it is easy to form a composite

with various materials or construct different types of heterojunctions [71–73]. As early as 2008, a $\text{TiO}_2/\text{V}_2\text{O}_5$ composite was prepared by Wang et al. [74] (Figure 4a), and the photoelectrochemical properties of $\text{TiO}_2/\text{V}_2\text{O}_5$ composites were studied in detail. In this work, TiO_2 exhibits a photo-response ability, while the UV light is irradiated to the $\text{TiO}_2/\text{V}_2\text{O}_5$ composite and a significant photocurrent is produced (maximum photon-to-current conversion efficiency is 37.1%). Meanwhile, V_2O_5 is considered to play a good role in energy storage, thanks to its Shcherbinaite structure and $\text{V}^{4+}/\text{V}^{5+}$ redox pair. The band structure diagram is shown in Figure 4b; the conduction band bottom of V_2O_5 is lower than that of TiO_2 , thus photo-generated electrons will flow downstream and accumulate in V_2O_5 forming the bronze structure and intercalating with H^+ or Li^+ ions ($\text{V}_2\text{O}_5 + x\text{e}^- + x\text{M}^+ \leftrightarrow \text{M}_x\text{V}_x^{4+}\text{V}_{2-x}^{5+}\text{O}_5$). This photocharging hybrid $\text{TiO}_2/\text{V}_2\text{O}_5$ material is predicted to become a photo-functional electrode for use in solar cells.

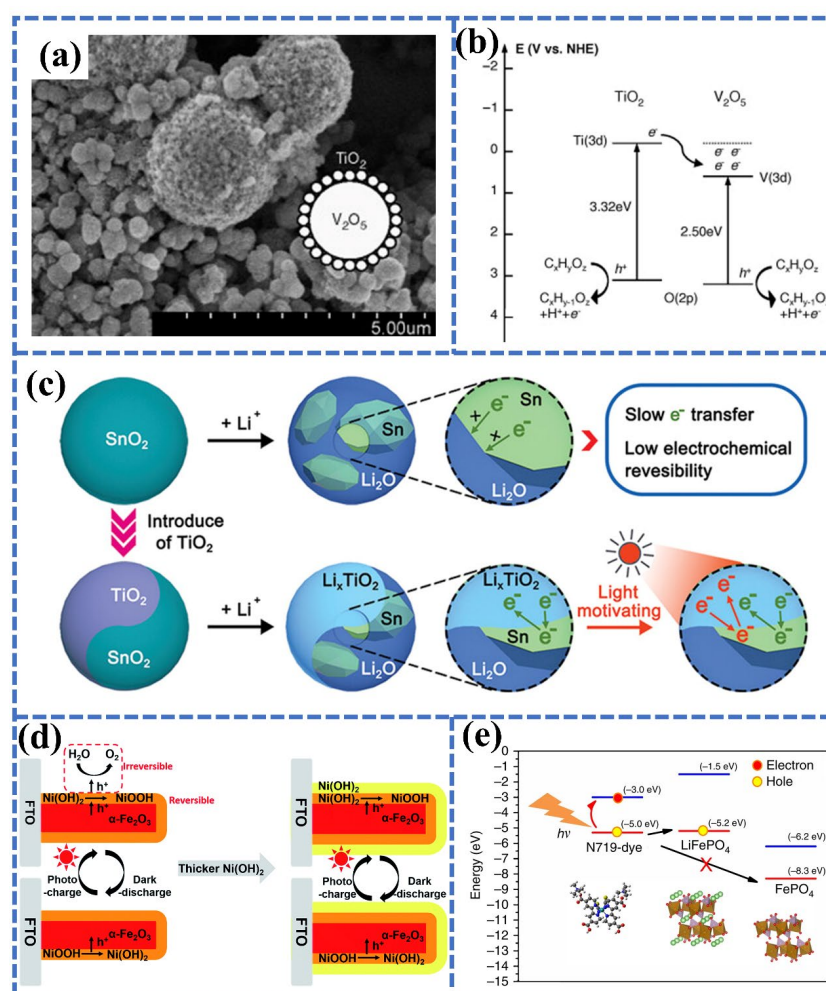


Figure 4. (a) SEM photographs and (b) schematic band energy diagram of the $\text{TiO}_2/\text{V}_2\text{O}_5$ composite. Reproduced with permission [74]. (c) The enhanced electrochemical reaction mechanism of photo-assisted device with the $\text{SnO}_2/\text{TiO}_2$ heterostructure electrode. Reproduced with permission [75]. (d) Schematic of photocharge and dark discharge process on $\text{Fe}_2\text{O}_3@/\text{Ni}(\text{OH})_2$. Reproduced with permission [76]. (e) Energy band alignment of the samples. Reproduced with permission [77].

Generally, many TiO_2 -containing composites adhere to the following mechanism: upon light irradiation, electron–hole pairs are generated in TiO_2 , holes are consumed on the electrode which suppresses the recombination of electron–hole pairs [78–81]. According to the above-mentioned mechanism, Yu Jihong et al. designed a $\text{TiO}_2\text{-Fe}_2\text{O}_3$ heterostructure cathode for photo-assisted Li-O_2 batteries, due to the heterojunction structure providing

a solution to address the problem of a high charge recombination rate in TiO_2 [82]. In 2021, a $\text{SnO}_2/\text{TiO}_2$ heterojunction was designed by Jiang Hao et al. as the anode for photo-assisted lithium-ion batteries [75]. Under illumination, Li_xTiO_2 ($x \geq 0$) is prone to generate electron–hole pairs, where electrons quickly flow into SnO_2 to promote its lithiation, and holes accelerate Li^+ migration to the TiO_2 , improving the kinetic performance. In the heterostructure cathode, TiO_2 is applied as a light-responsive and lithium storage material (Figure 4c). Thus, the $\text{SnO}_2/\text{TiO}_2$ heterojunction exhibits strong and stable photo-response current, and these PES LIBs show outstanding areal specific capacity and excellent cycling stability [75]. However, the semiconductor TiO_2 only absorbs light in the ultraviolet wavelength range, which severely limits the efficiency of photoelectric conversion and the practical application of devices.

Fortunately, Fe_3O_4 , as a more photosensitive material, has many advantages, including low cost, appropriate band gaps (1.9–2.2 eV), and electrochemical stability [83]. It could be combined with NiOOH as the cathode for the photo-assisted $\text{Li}-\text{O}_2$ battery with enhanced OER performance [53]. Luo et al. also designed an $\text{Fe}_2\text{O}_3@\text{Ni}(\text{OH})_2$ core-shell nanorod array as the photoelectrochemical electrode for a PES supercapacitor [76]. Fe_2O_3 as the light-responsive material absorbs solar energy and produces electron–hole pairs under light illumination. Meanwhile, $\text{Ni}(\text{OH})_2$, as the energy storage material, stores the photo-generated holes when the light is on; then, it releases electricity when the light is turned off (Figure 4d). This photoelectrochemical supercapacitor shows enhanced specific capacitance, and it could directly storage the solar energy which also paves the way for a deep understanding of the interface charge transfer between a photoelectrode and a battery-type capacitive material. In addition, CdS can couple with Pt or TiO_2 [84,85], as well as Si and the halide perovskite material being able to couple with WO_3 or NiCo_2O_4 to form a PES electrode with enhanced performance under light illumination [86,87].

In dye-sensitized solar cells and organic solar cells, the organic materials are also used as light capture agents constructing a multifunctional heterojunction PES electrode. For example, a N719 dye-hybridized LiFePO_4 composite (Figure 4e) was prepared by George Demopoulos and co-authors [77]. The N719 dye can absorb the visible light, and the LiFePO_4 is a universal lithium-ion battery cathode material. In the work of George et al., the N719 dye generates electrons and holes, while holes accumulate on the LiFePO_4 (the HOMO of N719 dye is higher than that of LiFePO_4) and oxidize LiFePO_4 into FePO_4 under light illumination. Therefore, in this light-assisted lithium-ion battery, the hybrid electrode can achieve the process of photocharging. Hyun-Kon Song and co-authors developed a photorechargeable battery with $\text{Li}_2\text{Mn}_2\text{O}_4$ in a dye-sensitized photoelectrode [88]. Excitingly, this battery has achieved an overall energy efficiency of up to 13.2%. In addition, a dye-sensitized $\text{TiO}_2\text{-Cu}_2\text{S}$ composite [89], and semiconducting polymers poly(3-hexylthiophene) (P3HT)-coated indium tin oxide branched nanowires (ITO BRs) [69] were also prepared for PES devices; under illumination, these materials transmit increased energy storage capacity. The strategy of combining photoelectric materials and energy storage materials results in the composites with both solar energy conversion and storage abilities. The arrangement of band structures at heterojunction component interfaces can promote the separation of photo-generated electrons and holes. Furthermore, the capacity, stability, and efficiency of the PES device based on heterostructure materials are significantly improved.

3. PES/Photo-Assisted Zinc–Air Batteries

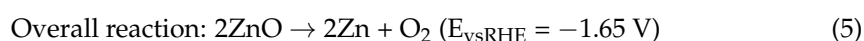
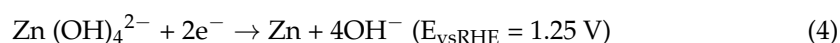
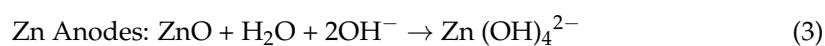
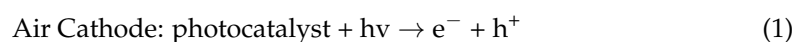
Zinc–air batteries (ZABs) possess the advantages of environmental friendliness, chemical stability, and low cost [90], which makes them an ideal alternative to lithium-ion batteries in the commercial field. In recent years, a number of light-assisted battery systems have undergone rapid development, such as photo-assisted LIBs/SIBs, photo-assisted

Li-air batteries, and photo-assisted supercapacitors. Meanwhile, photo-assisted Zn–air batteries have also aroused widespread interest among researchers, and the dual functional PES materials/photocathodes are research hotspots among the research into photo-assisted ZABs (PAZABs) [90–92]. Photocatalyst semiconductor materials such as the photocathode of PAZABs play a role in adjusting reaction pathways, reducing overpotential, and accelerating reaction kinetics. However, the single functionality, narrow light-response range, and high carrier recombination severely limit the practical application of semiconductor materials. Heterojunctions are the most popular photocathode materials, especially metal oxide-based heterogeneous (including metal oxides@metal oxides, metal oxides@metal sulfides, metal oxides@other porous materials, etc.).

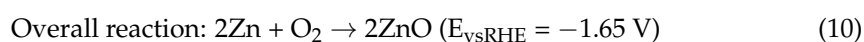
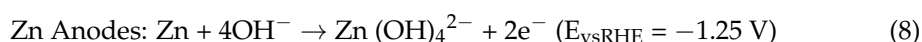
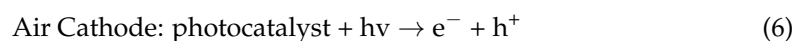
3.1. General Concept and Principles of PAZABs

Generally, PAZABs are a two-electrode cell system, comprising a zinc anode, a membrane, an electrolyte, and an air-/photo-electrode. To achieve high battery performance under illumination, the air electrode not only needs to have high catalytic activity and good air diffusion, but also excellent photo-responsive properties. A photo-assisted charging/discharging process is imported into the ZAB to accelerate ORR/OER kinetics and enhance overall performance. The fundamental charging/discharging mechanism of PAZABs is described in the following formulas [45]:

Charging process:



Discharge process:



Under illumination, photo-generated electron–hole pairs will be generated in the photocathode. Photo-generated electrons and holes can assist the charging/discharging processes.

Comparing PAZABs with commercially available lithium-ion batteries (LIBs), it can be seen that PAZABs have better energy storage performance and may lead the next generation of energy storage (Table 2) [45,93–96]. In terms of working mechanisms and core performance, PAZABs are characterized by the coupling of “light energy–electrical energy”. Their air cathodes rely on photocatalysts (such as g-C₃N₄, pTTh, and Fe₂O₃) to absorb photons and generate electron–hole pairs, which accelerate the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). During discharge, the zinc anode is oxidized to form Zn(OH)₄^{2−}. During charging, photoexcited holes drive the oxidation of OH[−] to release oxygen. There is no need for internal oxygen storage, and the batteries only rely on air for oxygen supply. In contrast, lithium-ion batteries only rely on electrical energy

to drive the intercalation and deintercalation of Li^+ between the positive and negative electrodes. Traditional liquid systems require liquid electrolytes for ion conduction, while all-solid-state systems use solid electrolytes such as LLZO and $\text{Li}_7\text{P}_3\text{S}_{11}$ instead of liquid electrolytes, and internal Li^+ storage is necessary to ensure charge–discharge cycles [93,94].

Table 2. Detailed comparison between PAZABs and LIBs.

Comparison Items	Photo-Assisted Zinc–Air Batteries [45,95,96]	Lithium-Ion Batteries [93,94]
Working Principle	Combines light energy and electrical energy; photocatalysts accelerate ORR/OER; relies on air for oxygen supply	Relies solely on electrical energy; Li^+ intercalation/deintercalation between positive and negative electrodes; requires internal Li^+ storage
Cost	Low raw material cost (zinc, low-cost catalysts), low preparation cost, and low system cost	Scarce lithium resources, positive electrodes contain precious metals, complex preparation of all-solid-state systems, and high cost
Efficiency	Round-trip efficiency of 60–87.7% with light assistance; maximum energy density of $1021.42 \text{ mWh g}^{-1}$	Round-trip efficiency of 80–90% for traditional liquid systems and 75–85% for all-solid-state systems; energy density of 400–600 Wh/kg
Lifespan	Decoupled cathode system: 1064 h of cycling (1596 cycles); two-electrode system: 1580 h of cycling	Traditional liquid system: 1000 cycles (70% capacity retention); all-solid-state Si-based system: 5000 cycles (61.5% capacity retention)
Temperature Adaptability	Operating range of $-25\text{ }^{\circ}\text{C}$ – $60\text{ }^{\circ}\text{C}$; photothermal effect mitigates low-temperature issues	All-solid-state system: $-60\text{ }^{\circ}\text{C}$ – $120\text{ }^{\circ}\text{C}$; traditional liquid system: $-20\text{ }^{\circ}\text{C}$ – $60\text{ }^{\circ}\text{C}$
Safety	No flammability risk, no internal oxygen storage explosion hazard; high-concentration KOH is corrosive	All-solid-state systems: no electrolyte leakage; traditional liquid systems: flammable; lithium dendrites may cause short circuits
Application Scenarios	Portable electronics, outdoor emergency power supplies, low-power devices	Electric vehicles, large-scale energy storage, extreme environment equipment

In terms of efficiency and cost, PAZABs benefit from the high abundance of zinc resources (70 mg kg^{-1} in the Earth’s crust) and low-cost photocatalysts (such as Fe_2O_3 and non-metallic $\text{g-C}_3\text{N}_4$). Their preparation process is simple, and no complex thermal management is required. With light assistance, the round-trip efficiency can reach 60–87.7%, and the maximum energy density is up to $1021.42 \text{ mWh g}^{-1}$ [45]. For lithium-ion batteries, however, the scarcity of lithium resources (20 mg kg^{-1} in the Earth’s crust) and the presence of precious metals such as Co and Ni in positive electrodes lead to higher costs. All-solid-state systems also require anhydrous and oxygen-free environments for the preparation of solid electrolytes and interface modification, which results in significantly higher costs. Although the efficiency of traditional liquid systems can reach 80–90%, their energy density is only 400–600 Wh kg^{-1} , and the efficiency of all-solid-state systems will further decrease to 75–85% due to interface impedance.

Regarding lifespan and environmental adaptability, the decoupled cathode system of light-assisted zinc–air batteries (pTTh for ORR and Fe_2O_3 for OER) can achieve stable operation for 1064 h (1596 cycles), and the cycle life of two-electrode systems can also reach 1580 h [96]. Lifespan degradation is mainly caused by zinc anode dendrites and electrolyte evaporation. Gel electrolytes (such as PANa-PVA-IL) can alleviate this problem by increasing water retention by 30%. Additionally, the photothermal effect enables the batteries to still cycle 642 times at $-25\text{ }^{\circ}\text{C}$ environment. At high temperatures, the high-temperature-resistant electrolyte ($6.0 \text{ M KOH} + 0.20 \text{ M Zn}(\text{Ac})_2$) has an ionic conductivity of 997 mS cm^{-1} at $80\text{ }^{\circ}\text{C}$, with an operating temperature range of $-25\text{ }^{\circ}\text{C}$ – $60\text{ }^{\circ}\text{C}$. For LIBs, the capacity retention rate of traditional liquid systems is approximately 70% after 1000 cycles. Although all-solid-state Si-based systems can cycle 5000 times (with a retention rate of 61.5%), their lifespan is greatly affected by lithium dendrites piercing the electrolyte, high-

temperature phase transitions of positive electrodes (such as the layered-spinel transition of LiCoO_2), and interface side reactions (such as the reaction between sulfide electrolytes and Li to form Li_2S). Nevertheless, all-solid-state systems can expand their low-temperature adaptation range to $-60\text{ }^\circ\text{C}$ through halide electrolytes (such as Li_3YCl_6). At high temperatures, they rely on Li_2ZrO_3 coating on positive electrodes to inhibit oxygen release, resulting in a capacity degradation of less than 8% after 300 cycles at $60\text{ }^\circ\text{C}$, and an overall wider operating temperature range (all-solid-state systems: $-60\text{ }^\circ\text{C}$ – $120\text{ }^\circ\text{C}$; traditional liquid systems: $-20\text{ }^\circ\text{C}$ – $60\text{ }^\circ\text{C}$).

As for safety and application scenarios, PAZABs use alkaline aqueous solutions or gels as electrolytes, posing no flammability risk. There is no need for internal oxygen storage, which avoids the risk of high-temperature oxygen explosion. Only high-concentration KOH electrolytes are corrosive. These batteries are more suitable for low-power situations such as portable electronic devices and outdoor emergency power supplies, and decoupled flexible batteries can be bent and support photo-assisted charging. For LIBs, all-solid-state systems have no electrolyte leakage issues and are safer than traditional liquid systems (liquid electrolytes are flammable). However, lithium dendrites may still cause short circuits by penetrating the grain boundaries of solid electrolytes [94]. With their relatively high energy density and wide temperature adaptability, lithium-ion batteries are more suitable for electric vehicles, large-scale energy storage, and equipment for extreme environments such as aerospace and polar exploration.

On the other hand, among photo-assisted metal air batteries, PAZABs still exhibit superior performances, especially compared to photo-assisted sodium air batteries (PASABs). Specifically, zinc is superior to sodium in electrochemical performance, resource cost, photo-assisted adaptability, and safety [95–97]. The standard redox potential of zinc is -0.76 V (vs. SHE), which has a high matching degree with the oxygen reduction reaction (ORR) potential of the air cathode, enabling it to reduce voltage polarization and improve energy efficiency. In contrast, the potential of sodium is -2.71 V (vs. SHE) [95], which has a large gap with the conduction band potential of most photocatalysts, requiring a higher external voltage for charging. Additionally, zinc exhibits excellent reversibility of deposition/dissolution in aqueous electrolytes. During discharge, the generated $\text{Zn}(\text{OH})_4^{2-}$ is converted to ZnO when saturated, and can be converted back to Zn during charging, with few side reactions. Sodium, however, tends to react with solvents in electrolytes, and even reacts with water to form NaOH and release H_2 in aqueous systems [98,99]. Such side reactions are difficult to inhibit even with photo-assistance, resulting in a short cycle life.

The crustal reserve of zinc is approximately 2.3×10^8 tons, with uniform distribution, and its production cost is only about USD 2.6 per kilogram. Although sodium has high crustal reserves, its production requires electrolysis of molten NaCl [99], which consumes a large amount of energy and costs about USD 20 per kilogram. In large-scale applications, the electrode material cost of zinc–air batteries is much lower than that of sodium–air batteries. Meanwhile, zinc purification technology is mature, and high-purity zinc can be obtained through pyrometallurgical or hydrometallurgical smelting. The discharge product ZnO is easy to recycle, with a recovery rate of over 95% [96]. The production of sodium requires inert gas protection; additionally, its discharge products are prone to deterioration, and the recycling process is difficult and causes high pollution. The bottleneck of zinc–air batteries lies in the slow kinetics of ORR/oxygen evolution reaction (OER) at the air cathode. Photo-assisted technology introduces photocatalysts (such as $\text{Au/g-C}_3\text{N}_4$ [95], $\text{Ag/Bi}_2\text{MoO}_6$), which can use photo-generated carriers to accelerate reactions and narrow the charge–discharge voltage gap. For SABs, the core problems are the side reactions of sodium and irreversible deposition. Photo-assistance can only accelerate some reactions and cannot fundamentally solve the problems. Moreover, the aqueous electrolytes commonly

used in ZABs have high ionic conductivity (0.1–0.3 S/cm) and good compatibility with photocatalysts, and most photocatalysts are stable in aqueous systems. In contrast, the non-aqueous electrolytes of sodium–air batteries have low conductivity, and photocatalysts are prone to react with electrolytes and lose their activity.

In terms of safety, ZABs are more reliable. Zinc has stable chemical properties and is not easily oxidized in air. Aqueous electrolytes have good thermal and chemical stability and are not easy to decompose or burn even when heated by light. Sodium is highly reactive and tends to react with O₂ and H₂O in air, so it needs to be isolated from air and moisture during storage and use. The non-aqueous electrolytes of SABs are prone to decomposition under light and high temperature, which may cause liquid leakage and fire, while zinc–air batteries do not have such risks [45,95]. In the future, with the optimization of photocatalysts and electrolytes, the performance of zinc–air batteries will be further improved, and they will have commercial potential in various fields. With the rapid development of PAZABs, standard testing protocols need to be established, and a minimal checklist of test requirements is proposed here (Table 3).

Table 3. A minimal checklist of testing protocols for photo-assisted ZABs.

Test Category	Test Item	Specific Requirements	Description
Light Intensity/ Spectroscopy	Light Source	A 300 W xenon lamp is used. An AM 1.5 G filter must be equipped for simulating sunlight; if no filter is used, full-spectrum irradiation should be clearly specified.	
	Measurement Position and Light Intensity	The measurement point is 1 cm away from the electrode surface; the light intensity is approximately 90 mW cm ^{−2} with a fluctuation range of ±5 mW cm ^{−2} .	
	UV-Vis Spectrophotometer Parameters	Test wavelength range: 300–800 nm (visible light absorption range); scanning rate: 200 nm min ^{−1} ; BaSO ₄ is used as the reference.	
Battery Structure/ Active Area	Liquid Battery Structure (Taking Zinc–Air Battery as an Example)	Anode: zinc foil; cathode: sample catalyst; electrolyte: liquid 6 M KOH + 0.2 M Zn(Ac) ₂ ; encapsulation uses a glass mold with an electrode spacing of 1 cm; continuous O ₂ purging (flow rate: 10 mL min ^{−1}) is maintained.	Stable and continuous O ₂ supply must be ensured to avoid interference from other components in the air with the electrolyte.
	Active Area Calibration	The edge sealing area and lead connection area must be excluded; cross-validation is required using the ImageJ (ImageJ 1.x series or ImageJ2) visual calibration method (error < 2%) and the weight back-calculation method (combined with catalyst loading, deviation < 5%).	Both calibration methods must be used simultaneously to ensure the accuracy of active area data.
Electrode Mass Loading (Taking Zinc–Air Battery as an Example)	Cathode Catalyst Loading	0.5–1 mg cm ^{−2}	The loading amount must be precisely controlled to avoid affecting the battery performance test results.
	Zinc Foil Parameters	Thickness: 50 µm; the mass change in the zinc foil before and after pretreatment must be recorded.	The mass change before and after pretreatment is a key indicator for evaluating the initial state of the zinc foil.
Basic Formula of Liquid Electrolyte Test	Preparation Method	Prepare 6 M KOH + 0.2 M Zn(Ac) ₂ using deionized water as the solvent. Stir at room temperature for 30 min until completely dissolved, then purge with O ₂ for 30 min to saturate the electrolyte.	Sufficient stirring is required to ensure complete dissolution of the solute, and O ₂ purging must last for an adequate time to ensure electrolyte saturation.
	Routine Test Temperature	25 °C, using a constant temperature chamber (fluctuation ± 0.5 °C).	Temperature stability must be maintained to reduce the impact of temperature fluctuations on test results.

Table 3. Cont.

Test Category	Test Item	Specific Requirements	Description
Temperature Range	Low-Temperature Test	Conducted in a low-temperature constant temperature chamber at a test temperature of $-10\text{ }^{\circ}\text{C}$.	
	High-Temperature Test	Test temperatures: $45\text{ }^{\circ}\text{C}$, $55\text{ }^{\circ}\text{C}$; the battery performance changes under different high temperatures must be recorded.	Focus should be placed on the impact of high temperatures on battery stability and performance.
Cycling Protocol	Cycling Stability Test	The structural stability of the battery after 50 cycles must be recorded.	50 cycles is the minimum test standard, which is used to evaluate the long-term service potential of the battery.
Test Conditions	Test Equipment and Mode	Equipment: LAND-CT2001A battery testing system; test mode: constant current charge–discharge.	
	Current Density Range for Liquid Battery	$0.1\text{--}2\text{ mA cm}^{-2}$	An appropriate current density within this range should be selected for testing to cover different application scenarios.
	Cut-Off Voltage	Charging upper limit: 2.0 V vs. RHE; Discharging lower limit: 0.8 V vs. RHE.	The cut-off voltage requirements must be strictly followed to prevent battery damage caused by overcharging and over-discharging.
	Lighting Conditions	Equipped with an AM 1.5 G filter; Light intensity: 90 mW cm^{-2} ; the illuminated area must cover the entire active area.	The illuminated area must be completely matched with the active area to avoid uneven local illumination.
	Auxiliary Tests	A three-electrode system is used to evaluate ORR/OER performance; Linear Sweep Voltammetry (LSV) is performed at a scanning rate of 2 mV s^{-1} ; the Rotating Ring-Disk Electrode (RRDE) is operated at a rotation speed of 1600 rpm.	Auxiliary tests are used to conduct in-depth analysis of the electrode reaction process and supplement the overall battery performance data.
Timing Modes	Continuous Lighting Mode	A light intensity of 90 mW cm^{-2} is maintained during both charging and discharging stages; turn on the light 5 min in advance and turn it off 3 min after discharging ends.	The light-on and light-off times must be precisely controlled to ensure synchronization between the lighting and the charge–discharge process.
	Intermittent Lighting Mode	Cycle duration: 20 min (10 min of lighting/10 min of darkness) with a duty cycle of 50%; the charging voltage changes under different timings must be recorded.	Focus on the fluctuation of charging voltage when switching between darkness and lighting.

3.2. Photocathode Materials for PAZABs

TiO_2 , as an n-type semiconductor rich in oxygen vacancy defects, can serve as an electron donor, and it is also a promising photocatalyst for photo-assisted ZABs (PAZABs). Under light illumination, single-component TiO_2 only can facilitate the OER process. Combining TiO_2 with other materials can achieve dual-functional (ORR and OER) catalysis. In 2023, Xue et al. synthesized a step-scheme (S-scheme) $\text{TiO}_2\text{-In}_2\text{Se}_3$ heterojunction air cathode [100]. Under illumination, the photo-generated electrons are transferred from the conduction band (CB) of TiO_2 to the valence band (VB) of In_2Se_3 , a process powered by the internal electric field (IEF). As shown in Figure 5a, under illumination, the electrons remain in the CB of In_2Se_3 and undergo a reduction reaction with O_2 to form $\cdot\text{O}_2^-$ on the surface of catalyst, which subsequently reduces $\cdot\text{O}_2^-$ to OH^- , during the process of discharge. Meanwhile, the theoretical discharge voltage is the potential difference between the VB of TiO_2 and Zn/ZnO , which is higher than the equilibrium voltage of ZABs in the dark (1.64 V). During discharging, the holes remain in the VB of TiO_2 and undergo an oxidation reaction with OH^- to form $\cdot\text{OH}$; then, $\cdot\text{OH}$ breaks down further to produce O_2 . In this case, the theoretical charge voltage is equal to the potential difference between the CB of In_2Se_3 and Zn/ZnO . Thanks to the existence of S-scheme heterojunctions, carriers with

different electrical properties are more likely to separate and exist in the VB of TiO_2 and the CB of In_2Se_3 , promoting OER and ORR, respectively.

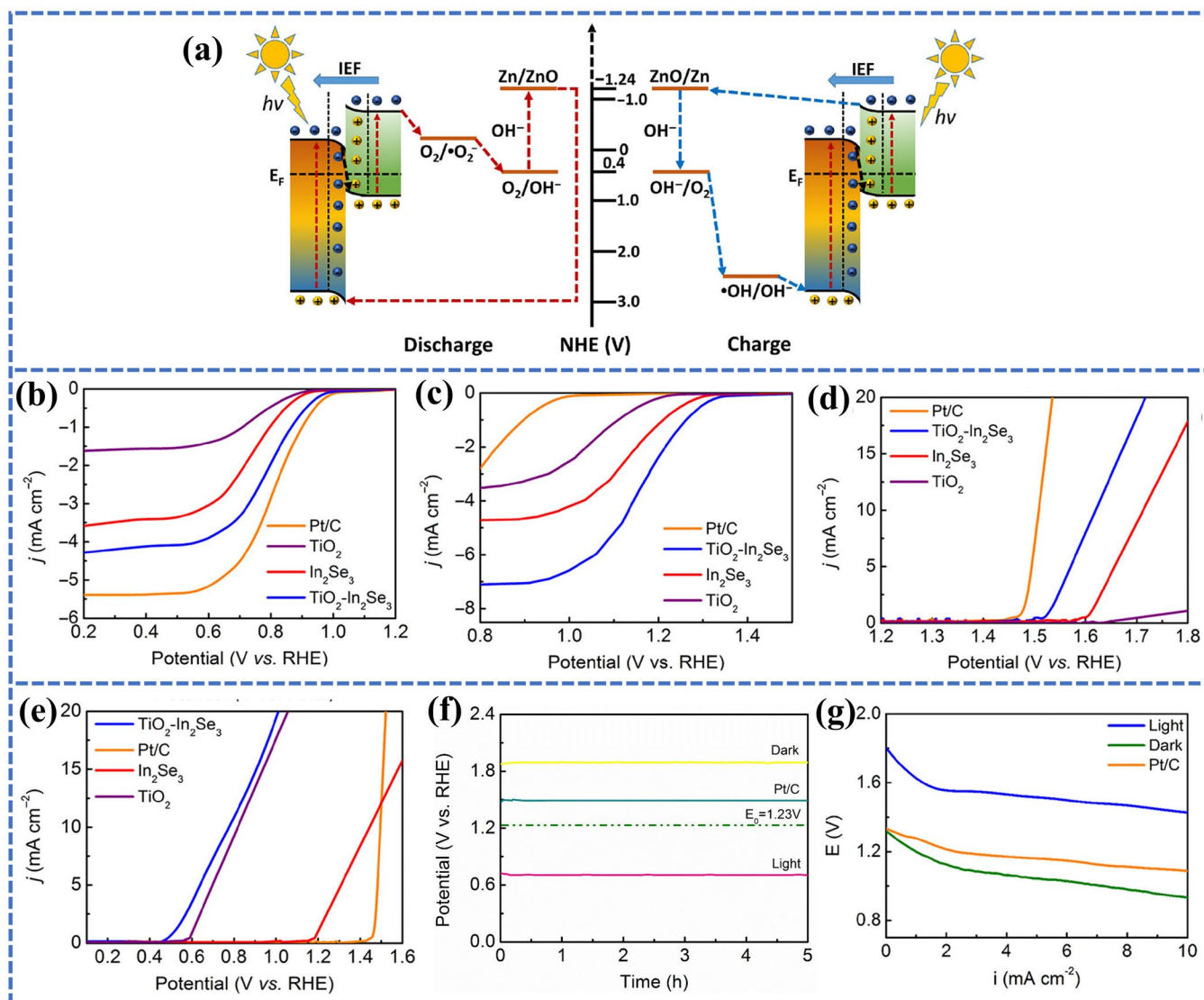


Figure 5. (a) The working mechanism of S-scheme $\text{TiO}_2\text{-In}_2\text{Se}_3$ heterojunction during the discharge and charge processes, under illumination. ORR polarization curves of catalysts at a scan rate of 5 mV s^{-1} , (b) under illumination, and (c) in dark. OER polarization curves of catalysts (d) under illumination and (e) in dark. (f) Polarization curves of $\text{TiO}_2\text{-In}_2\text{Se}_3$ with and without light irradiation in comparison with Pt/C. (g) Discharge curves of the Pt/C-based ZAB and $\text{TiO}_2\text{-In}_2\text{Se}_3$ -based ZAB (under illumination and dark) at a sweep rate of 0.01 mA s^{-1} . Reproduced with permission [100].

Therefore, in experiments, $\text{TiO}_2\text{-In}_2\text{Se}_3$ electrodes have a higher charging voltage and lower discharge voltage than Pt/C electrodes. In detail, the ORR and OER activities of the $\text{TiO}_2\text{-In}_2\text{Se}_3$ cathode and Pt/C are investigated using the same three-electrode system under identical conditions. As shown in Figure 5b,c, during the ORR process the onset potential of $\text{TiO}_2\text{-In}_2\text{Se}_3$ (1.28 V) under illumination is higher than in the dark (0.96 V) and also higher than that of Pt/C (0.99 V). The slopes of Tafel curves of catalysts under illumination are larger than in the dark, showing better ORR kinetics during light exposure. The OER curves of catalysts are shown in Figure 5d,e. $\text{TiO}_2\text{-In}_2\text{Se}_3$ heterojunction exhibits the lowest OER onset potential (0.48 V) than without illumination and Pt/C (1.47 V). The Tafel curves of catalysts of OER illustrate that light illumination can enhance the OER kinetics. The ORR

and OER activity stabilities are monitored for up to 5 h, and the $\text{TiO}_2\text{-In}_2\text{Se}_3$ heterojunction exhibits good stability under illumination and dark (Figure 5f). As for ZABs, during the discharging process, the discharge voltage of the $\text{TiO}_2\text{-In}_2\text{Se}_3$ -based ZAB upon light irradiation is higher than that in the dark and also higher than that of the Pt/C-based ZAB (Figure 5g). The incident monochromatic photon-electron conversion efficiency (IPCE) [45] of ZABs at different current densities shows that the value of IPCE gradually increases with increasing current density, until the current increases sharply. The diminishing of IPCE is mainly attributed to the lifetime of the photo-generated carriers in the cathode not being sufficient for the multi-electron transfer process of the ORR/OER [45,100].

In addition, $\alpha\text{-Fe}_2\text{O}_3$ has also been proven to be a suitable semiconductor photoelectrode material, due to its appropriate band structure ($E_g = 2.10$ eV) and excellent photoelectric stability. As early as 2019, Hu et al. [64] developed a photo-assisted zinc–air battery with $\alpha\text{-Fe}_2\text{O}_3$ as the air photoelectrode. This group innovatively proposed that the band structure and photoelectrochemical stability of $\alpha\text{-Fe}_2\text{O}_3$ are the key factors determining the charging performance of photo-assisted zinc–air batteries. As a result, the $\alpha\text{-Fe}_2\text{O}_3$ -based photo-assisted ZABs show a low initial charge potential of -1.43 V, under illumination, which is lowered by around 0.5 V compared to the charge voltage of conventional ZABs. They proposed that under light illumination, the charging process undergoes significant changes. Specifically, the generation and transfer of photo-generated carriers promote the dynamic performance of the OER process, reducing the charging voltage. As shown in Figure 6a, the photo-generated electrons are injected into the CB of the photoelectrode, then it transfers to the Zn anode by external circuit, participating in the reduction reaction. At the same time, photo-generated electrons transfer to the surface of the photocathode to participate in oxidation reactions. In order to better understand the mechanism of sunlight-promoted charging process, the BiVO_4 -based PAZABs were also investigated. Figure 6b illustrates that the photo induced voltage compensates for the high charging potential of the ZAB. And the theoretical sunlight-promoted charge potential equals the potential difference between the $\text{Zn(OH)}_4^{2-}/\text{Zn}$ redox potential and the quasi-Fermi level of electrons. Thus, they believe that the band structure of BiVO_4 and $\alpha\text{-Fe}_2\text{O}_3$ significantly affects the charging performance of the PAZABs. Similar to metal oxides, metal sulfides have suitable energy band structure and electrochemical/photochemical stability [101]. A p-type NiCo_2S_4 photocatalyst was developed by the group of Sarawutanukul [102]; under irradiation, this photocatalyst delivers reduced OER and ORR overpotential. In addition, the NiCo_2S_4 cathode can decrease the potential gap and increase the round-trip efficiency of the ZAB.

Polymer semiconductor catalysts with adjustable energy band structures and broad light absorption make them an ideal air cathode for PAZABs. Researchers have found that several photosensitive polymers, including poly(trithiophene) (pTTh), poly(1,4-di(2-thienyl)) benzene (PDTB), polyaniline nanorod arrays (PANINA), and triazine-based conjugated polymers, can be used as catalysts to prepare light-assisted ZABs [66,91]. Typically, the pTTh, as a p-type polymer semiconductor, can be prepared by simple and convenient methods, and it has a wide absorption range, as well as strong light stability, which allows it to fully utilize solar energy. For example, Li et al. [91] used pTTh as the cathode to prepare the photo-assisted ZAB, achieving direct storage of solar energy into electrical energy, in 2019. Under illumination, photo-generated electron–hole pairs will be generated and separated in the pTTh semiconductor catalyst. The photo-generated electrons are excited to the CB of pTTh then injected into the π_{2p}^* orbitals of O_2 for its reduction reactions, while the holes in the VB of pTTh are transferred to the Zn anode through the external circuit and participate in the oxidation reaction of Zn to ZnO. Upon illumination, the theoretical output voltage of Zn–air batteries can be raised by 0.82 V to reach 2.46 V.

This work also reveals that the ORR reaction actually undergoes a $2e^-$ pathway, resulting in an output voltage of 1.78 V at 0.1 mA cm^{-2} experimentally, which is higher than the thermodynamic limit of 1.64 V without illumination in ZABs. Furthermore, the pTTh air cathode exhibits better stability and higher energy density than the Pt/C cathode in ZABs. This work inspired further exploration of pTTh cathodes for photo-assisted ZABs.

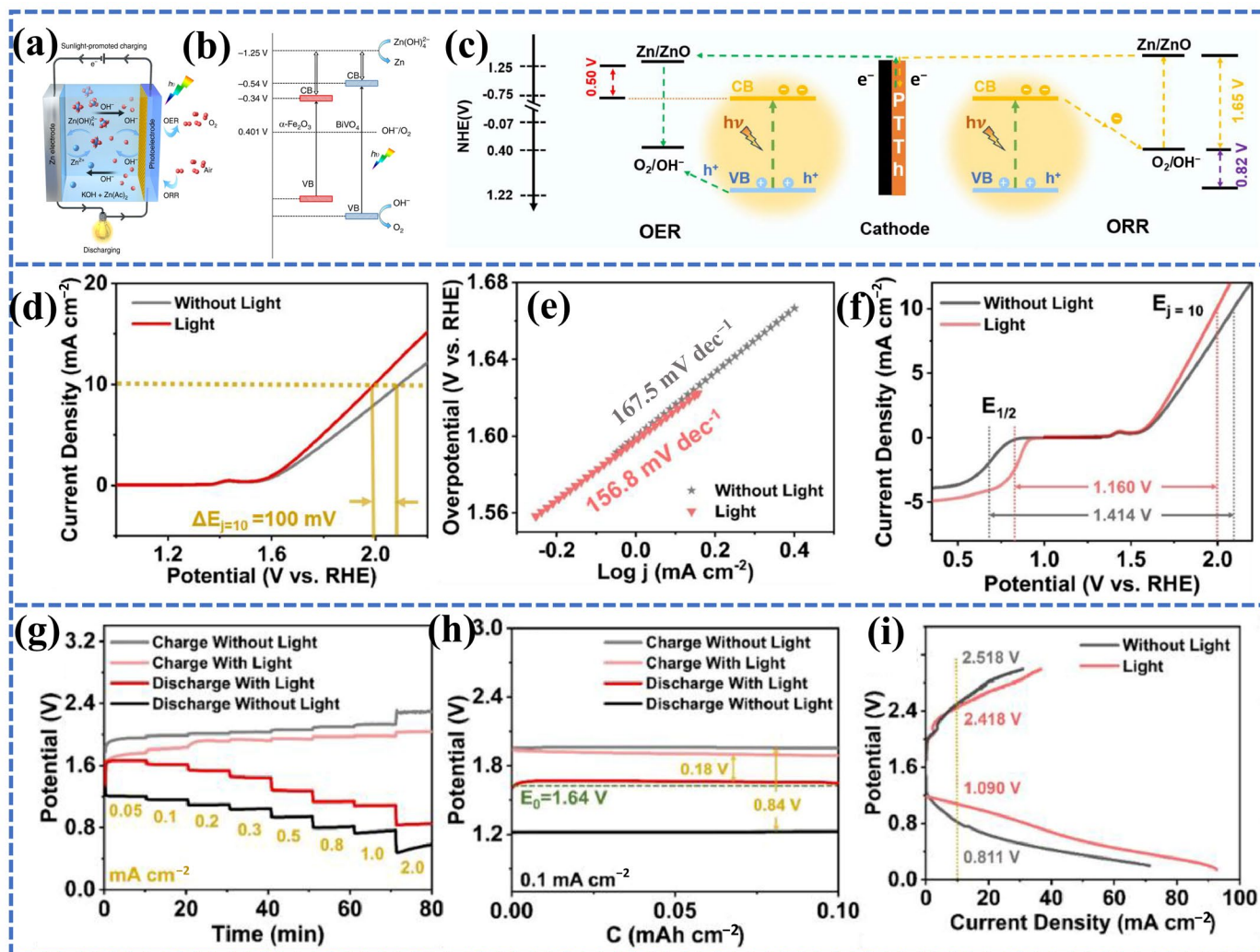


Figure 6. (a) The structure and working principle of the photo-promoted ZAB, and (b) the mechanism of the photo-promoted charging process under illumination. Reproduced with permission [64]. (c) ORR/OER mechanism diagram of photo-assisted pTTh/CCB cathode-based ZABs. (d) LSV and (e) Tafel slope of pTTh with/without illumination for OER, (f) LSV overall curves for ORR and OER including the ΔE between $E_{1/2}$ and $E_j = 10$. Photoelectrochemical performances of pTTh/CCB cathode-based ZABs with/without illumination: (g) charge-discharge profiles at current densities from 0.05 to 2.0 mA cm^{-2} , (h) charge/discharge profiles of at 0.1 mA cm^{-2} , (i) polarization curves at 1 mV s^{-1} . Reproduced with permission [103].

For example, Hu et al. [103] in 2024, prepared a bifunctional pTTh catalyst by electrochemical synthesis method, and the pTTh catalyst was used as a flexible cathode for PAZABs. The pTTh electrode exhibits both ORR and OER catalytic activity. Thus, the performance of both charging and discharging processes is improved due to the effect of light illumination. During the charging process, photo-generated electrons and holes separate and transfer on the CB and VB of pTTh semiconductor catalyst, promoting the corresponding catalytic processes, respectively (Figure 6c). Photogenerated holes participate

in the ORR process, and photo-generated electrons are injected into the CB of the catalyst and transferred to the zinc anode through an external circuit, participating in the reduction of Zn^{2+} to produce Zn. As shown in Figure 6c, the photo-generated electrons and holes promote OER and reduce the charge potential, in charge process. During the discharge process, photo-generated electrons participate in reduction reactions (ORR), reducing O_2 to OH^- . Simultaneously, photo-generated holes transfer to Zn anode through the external circuit, participating in oxidation reaction and forming ZnO. Due to the light-assisted effects, ORR is promoted, and the discharge potential is increased.

Under light illumination, the onset potential and half-wave potential of photo-assisted pTTh electrode are 0.91 V vs. RHE and 0.83 V vs. RHE, which are better those in dark (0.82 V vs. RHE and 0.68 V vs. RHE), revealing the enhanced ORR performances of the pTTh electrode under illumination. And the diffusion current density of the pTTh electrode is also higher with illumination (4.43 mA cm^{-2}) than without illumination (2.04 mA cm^{-2}) at 0.7 V. The E_{10} is 1.99 and 2.09 (Figure 6d), corresponding to situations with/without illumination, respectively, indicating a significantly reduced overpotential (100 mV) of pTTh under illumination. The Tafel slope is also smaller with illumination ($156.8 \text{ mV dec}^{-1}$) than without illumination ($167.5 \text{ mV dec}^{-1}$) (Figure 6e). The ΔE is 1.160 V vs. RHE under illumination, which is lower than 1.414 V vs. RHE in dark (Figure 6f). And the small value of ΔE under illumination indicates the improvement in ORR and OER performance by illumination. Correspondingly, the enhancements of ORR and OER by illumination result in the better performance of the ZABs under illumination than in the dark. The electrochemical performance of pTTh/CCB cathode-based ZABs is investigated. The charge/discharge potential of the pTTh/CCB cathode-based ZAB at different current densities is shown in Figure 6g. The discharge and charging potentials under illumination increased by 41.74% and 9.04%, respectively, compared to the discharge and charging potentials in the dark, at a current density of 0.1 mA cm^{-2} ; indicating that the impact of illumination on ORR is more pronounced than OER. In addition, as the current density increases, the influence of illumination on the ORR/OER potential gradually weakens.

The charge/discharge curves (1 h) of pTTh/CCB cathode-based ZABs under illumination/in the dark are shown in Figure 6h. The discharge potential with illumination is 1.63 V close to the equilibrium potential (1.64 V) and higher than without illumination (1.15 V). The charge potential with illumination is 1.81 V, nearing that of commercial Pt/C + RuO_2 cathode-based ZABs (1.8 V), lower than without illumination (1.99 V). Therefore, the ΔE of pTTh/CCB cathode-based ZABs under illumination is 0.18 V, which is lower than the ΔE in the dark (0.84 V), and lower than the ΔE of Pt/C + RuO_2 cathode-based ZAB (0.43 V), corresponding to a highest round-trip efficiency of 90.06%. The charge–discharge polarization curves show that the charge–discharge gap of a ZAB with illumination is narrower than that of a ZAB without illumination (Figure 6i). The specific capacity of photo-assisted pTTh/CCB cathode-based ZABs is $553.38 \text{ mA h g}^{-1}$ and the energy density is $681.71 \text{ W h kg}^{-1}$. Generally speaking, in their work, the pTTh photocathode not only exhibits dual function catalysis, but also has significant stability and charge–discharge performances. As a result, a single photo-assisted ZAB with pTTh cathode can power a diode or a toy car, as well as four PAZABs in series being able to charge a smartphone. Thus, this work has realized the practical and flexible application of PAZABs, paving new avenues for the development of efficient and green energy.

3.3. Decoupled Cathode PAZABs

The ORR and OER reactions of the cathode inherently have conflicting operational requirements. To promote air diffusion and prevent active site blockage, ORR reactions typically require catalyst surfaces with a hydrophobic character [104]. However, to facilitate

gas–liquid–solid interfacial reactions and oxygen release, OER generally demand a catalyst with hydrophilic properties [105]. In addition, another significant difference between ORR and OER is the operational potential, with OER having a higher operational potential than ORR [106]. Operating at the elevated potential will damage the structure and chemical properties of the catalyst, as well as affecting the ORR activity under high discharge current [107]. And so far, the decay mechanism of ORR catalyst at high OER potential is still unclear. On this occasion, to overcome the significant obstacles of bifunction air catalysts in two-electrode systems, the three-electrode ZAB has stimulated extensive research studies.

Recently, Hu et al. [96] developed a light-assisted decoupled cathode ZAB system, with a zinc anode and two semiconductor cathodes (Figure 7a). In their work, polyterthiophene (pTTh) and Fe_2O_3 were selected as catalysts for ORR and OER, respectively, to verify the effectiveness of the decoupling strategy. The pTTh possesses excellent conductivity, good compatibility with the electrolyte, and outstanding catalytic activity, enabling efficient electron transport, reduced interface resistance, and reaction facilitation during ORR, while maintaining structural stability at low potential [108]. Cost-effective Fe_2O_3 , as another cathode, shows excellent chemical stability, resisting degradation during OER, thereby prolonging the battery's lifespan. In addition, the Fe_2O_3 cathode demonstrates the capability of effectively lowering the OER overpotential and facilitating oxygen evolution [109]. In this strategy, the decoupled cathodes enable operation under their optimal conditions, allowing for efficient performance under high current operation (Figure 7c). Under illumination, the three-electrode system exhibits excellent cycling stability (1064 h at 5 mA cm^{-2}), outstanding lifespan (1596 cycles), and high energy density ($1021.42 \text{ mWh g}^{-1}$). Thanks to the cathodic decoupling strategy, ZABs can operate stably in harsh environments across a broad temperature range (Figure 7b), paving a new way for enhancing the adaptability and stability of ZABs.

In PAZABs, solar irradiation can facilitate OER kinetics, thus reducing the charge potential [45,110,111]. And the charge voltages depend on the potential difference between the conduction band (CB) bottom of the semiconductor photoelectrode and the $\text{Zn}/\text{Zn}(\text{OH})_4^{2-}$ redox potential on the anode. Based on these, the energy levels of the photoelectrode need to match with the Zn redox pair. Generally, a low potential at the CB bottom is necessary to ensure a small theoretical charge voltage, and a high potential at the valence band (VB) top is needed to provide strong oxidation ability. Wide bandgap semiconductors (such as TiO_2) have appropriate positions for CB and VB, which can reduce the photo-assisted charging voltage. However, the band gap of 3.2 eV of TiO_2 corresponds to the ultraviolet light-response, which hinders the practical application of the device under the visible light irradiation [66,110]. Semiconductors with narrower bandgaps can efficiently absorb visible light, but a more positive potential at the CB bottom means the larger theoretical charge voltage, and a more negative potential at the VB top weakens the oxidation ability, causing a sluggish OER kinetic process [91]. Therefore, defect (oxygen vacancy) engineering and heterojunctions construction have been employed to regulate the photoelectrocatalytic activity of the air cathode [49,66,112]. But the regulatory mechanisms of oxygen vacancies and the role of the heterojunction interfaces have not been sufficiently explored and understood.

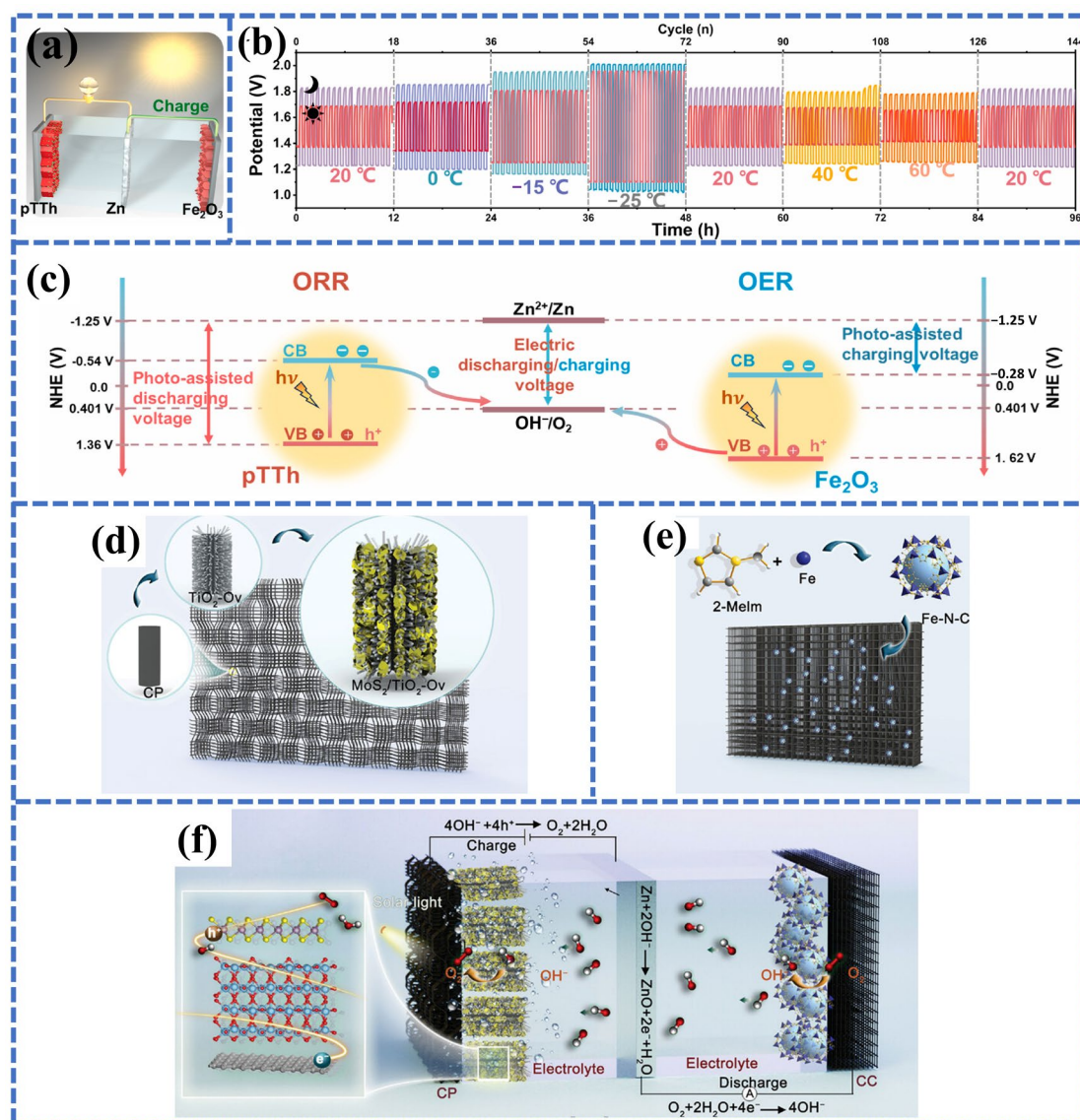


Figure 7. (a) Structure diagram of photo-assisted dual-cathode ZAB, (b) charge and discharge curves of F-pTTh || Zn || Fe₂O₃ under different temperatures with and without illumination, (c) schematic diagram of photo-assisted ZABs. Reproduced with permission [96]. The preparation process of (d) MoS₂/TiO₂-O_v heterojunction and (e) FeNC, (f) the mechanism of charging/discharging processes of the photo-assisted ZABs. Reproduced with permission [46].

Inspired by the energy level matching relationship between the semiconductor photo-electrode and the Zn redox pair, a three-electrode system is urgently needed, incorporating two cathodes: one allows a greater number of photo-generated holes to participate in the OER, and another possesses the ability to strongly interact with O₂, delivering superior ORR catalytic activity. Wu and his co-workers [46], using an MoS₂/oxygen vacancies-rich TiO₂ heterojunction as the charge cathode and Fe, N-doped carbon matrix (FeNC) as the discharge cathode, constructed a three-electrode photo-assisted ZAB (Figure 7d–f). Considering the effect of bandgap on photocatalytic activity, MoS₂ with a narrow band gap (around 1.6 eV) is chosen as solar light-responsive catalytic material and TiO₂ (band gap around 3.2 eV) acts as the electron transport layer and hole-blocking layer, constructing an MoS₂/oxygen vacancies-rich TiO₂ heterojunction as the charge cathode and Fe, N-doped carbon matrix (FeNC) as the discharge cathode. Defect engineering in TiO₂ facilitates the temporary trapping of carriers and triggers rapid carrier transfer at the heterostruc-

ture interface, which hinders the recombination of photo-generated electron–hole pairs. Thereby, abundant holes can further participate in the OER, promoting kinetic processes. Meanwhile, strong d- π interactions exist in the FeNC cathode, promoting the ORR of ZABs. Consequently, under illumination, such three-electrode ZABs demonstrate a significant reduction in charge voltage during the charging process. And in a dark environment, this system also shows a high discharge voltage (~ 1.32 V at 0.5 mA cm^{-2}) and superior power density (167.6 mW cm^{-2}). This work inspired researchers to perform charging and discharging processes on separate cathodes. Thus, this ensures an excellent thermodynamic environment and enhanced kinetics of OER, with an efficient ORR regardless of light exposure. Overall, the three-electrode system is beneficial for overcoming the contradiction between ORR and OER, which is expected to light up new directions for the development of ZABs.

In addition, the role of oxygen vacancy/defect engineering in adjusting the light absorption and charge transport properties of photocathodes in PAZABs was thoroughly researched by Wu et al. [46]. In order to reveal the regulatory mechanisms of oxygen vacancies and heterojunction interfaces for photoelectrochemical properties, a series of characterizations are implemented, including Kelvin probe force microscopy (KPFM), atomic force microscopy (AFM), time-resolved photoluminescence (PL) spectra and EPR measurements. Firstly, the combination of in situ irradiated XPS spectra, KPFM, and AFM measurements can reveal electron transfer and electron transfer pathways in heterostructures with oxygen vacancies, demonstrating the role of oxygen vacancy in carrier dispersion and transfer under dark and light illuminations (Figure 8a–f) [46]. Consequently, vacancies can facilitate the separation kinetics of charge carriers, effectively preventing the combination of photo-generated electron and hole. Secondly, time-resolved PL spectra (Figure 8g) [113] combined with the Shockley–Read–Hall (SRH) model [114] can reveal that the oxygen vacancy energy levels can temporarily capture and subsequently release carriers, thus obstructing the recombination of carriers under illumination. Finally, introducing oxygen vacancies into the heterojunction electrode targets the generation of oxygen vacancy energy levels for temporarily capturing carriers and weakening the built-in electric field at the heterojunction interface, hindering carrier recombination and permitting more photo-generated holes to participate in OER. In addition, EPR measurements are conducted to detect hydroxyl ($\cdot\text{OH}$) during the OER process under illumination. Figure 8h,i show that $\text{TiO}_2\text{-O}_v$ possesses a much stronger signal intensity of $\cdot\text{OH}$ than TiO_2 , and the signal intensity of $\cdot\text{OH}$ in $\text{MoS}_2/\text{TiO}_2\text{-O}_v$ heterojunction is strongest among $\text{TiO}_2\text{-O}_v$, MoS_2 , and $\text{MoS}_2/\text{TiO}_2$. This indicates that the regulation of O vacancies in $\text{TiO}_2\text{-O}_v$ and $\text{MoS}_2/\text{TiO}_2\text{-O}_v$ samples efficiently inhibits the recombination of photo-generated electrons and holes, allowing a larger number of photo-generated holes to participate in OER, forming an enhanced signal of intermediate $\cdot\text{OH}$ (Figure 8h,i). On the other hand, Zhang et al. demonstrated that oxygen vacancy can increase the durability of photo-assisted metal–air batteries [115]. Due to the presence of oxygen vacancies, the inert surface and low conductivity of the photoelectrode material can be weakened. Under illumination, a large number of electrons and holes can be generated in situ, reducing the charge and discharge overpotentials and improving the recoverability of the catalyst, thereby enhancing energy storage efficiency and durability of the photoelectrode rich in oxygen vacancies.

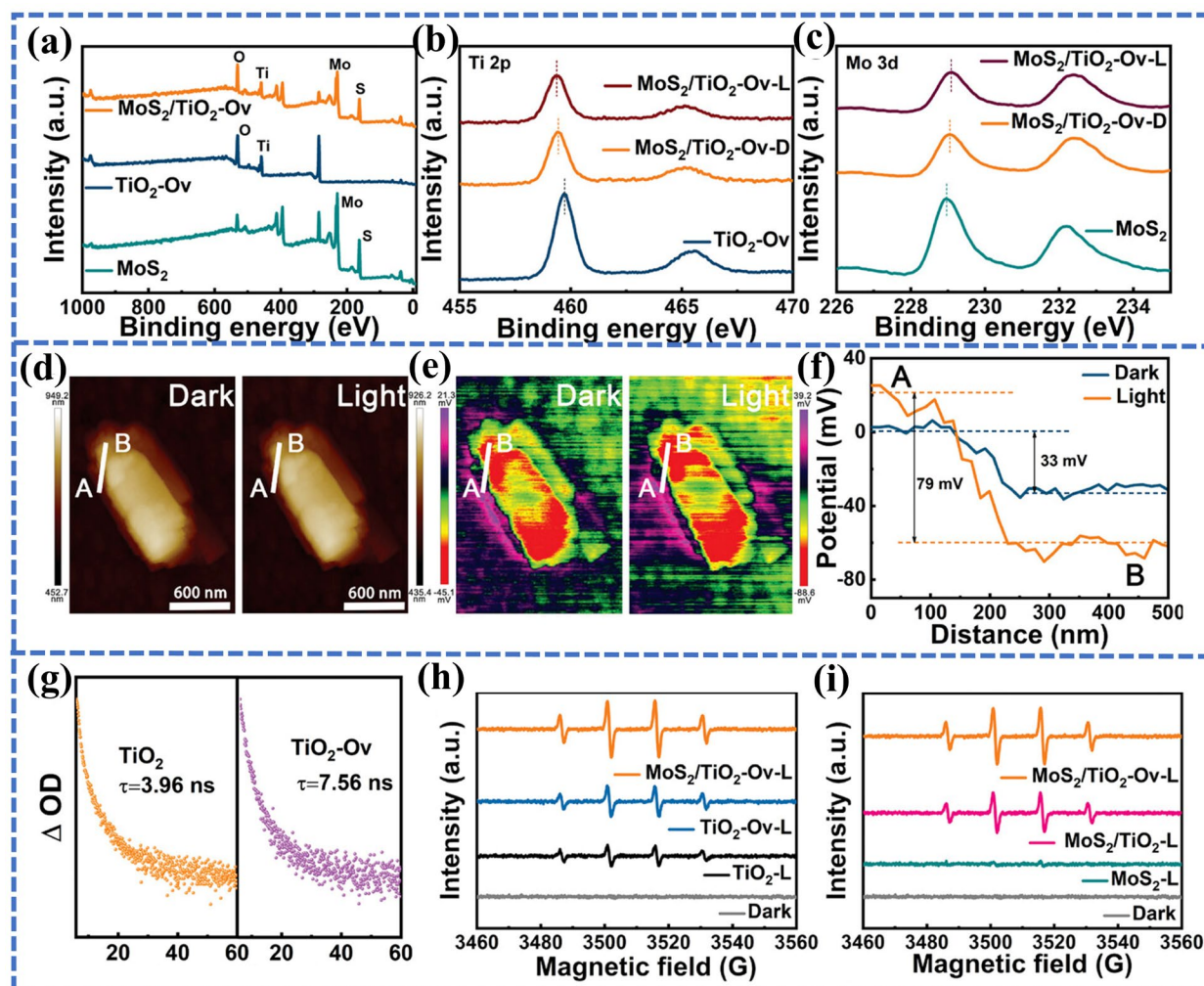


Figure 8. XPS spectra of $\text{TiO}_2\text{-O}_v$, MoS_2 , and $\text{MoS}_2/\text{TiO}_2\text{-O}_v$ samples: (a) the XPS survey spectra, (b) high-resolution XPS spectra of Ti 2p, and (c) high-resolution XPS spectra of Mo 3d. (d) AFM image of $\text{MoS}_2/\text{TiO}_2\text{-O}_v$ in dark and under illumination, (e) the corresponding surface potential image of KPFM, and (f) the line-scanning surface potential from A to B in inset (f). (g) Time-resolved PL spectra of TiO_2 and $\text{TiO}_2\text{-O}_v$. (h) EPR spectra of TiO_2 , $\text{TiO}_2\text{-O}_v$, and $\text{MoS}_2/\text{TiO}_2\text{-O}_v$, and (i) EPR spectra of MoS_2 , $\text{MoS}_2/\text{TiO}_2$, and $\text{MoS}_2/\text{TiO}_2\text{-O}_v$. Reproduced with permission [46].

4. Interface Engineering of Photocathode Materials

Benefiting from the significant interfacial interaction, electron-rich and electron-deficient regions are simultaneously exposed in heterostructure catalysts, which helps to achieve dual function (ORR and OER) catalysis. Furthermore, some transition-metal-based heterostructure catalysts even display higher activity and stability than noble metal-based catalysts in ZABs [12,116,117]. In heterostructures, the direct contact between two components, owing to differences in their Fermi levels, geometric structures, and electron affinities, triggers unique interfacial properties, which are key to enhancing catalytic performance [3]. As stated previously, specifically, the following applies: 1. Charge Redistribution: Fermi level disparities induce built-in electric fields at the interface, leading to charge (electrons and holes) redistribution. Separated charges facilitate ORR and OER processes, improving reaction efficiency and kinetics. 2. Lattice Strain: Mismatches in geometric structure and lattice constants generate compressive or tensile strain at the interface, causing d-band center shifts and defect formation. 3. Chemical Bonding: Differences in electron affinity form interfacial chemical bonds, enabling electron transfer through these bonds. These factors primarily enhance the catalytic activity of heterostructure bifunctional catalysts by modu-

lating electronic structures in ZABs. As for PAZABs, which combines electrochemistry and photochemistry in its reaction mechanism [13,29], photoelectrochemical energy storage cathode material in it is a key component. The efficient charge separation at heterogeneous interfaces also plays an important role in improving photo-assisted ZAB performances.

4.1. Interface Engineering Towards Heterojunction Photocathode

Generally, semiconductor–semiconductor heterojunctions can be classified into three types based on the relative positions of CB and VB, including straddling gap (type I), staggered gap (type II), and broken gap (type III) [28,118]. As shown in Figure 9a, the VB of semiconductor B lies higher than that of semiconductor A, while the CB of semiconductor B lies lower than that of semiconductor A, which is named straddling gap (type I) heterojunction. Under the condition of type I, both the photo-generated electron and holes will transfer from the CB and VB of semiconductor A to the CB and VB of semiconductor B, respectively. Consequently, under illumination, type I heterojunctions cannot achieve effective separation of photo-generated electrons and holes. Figure 9b shows the band arrangement of the staggered gap (type II) heterojunction, and both the CB and VB of semiconductor B lie lower than those of semiconductor A. Under this condition (type II), when illumination occurs, electrons will transfer from A (CB) to B (CB), and holes will accumulate in the VB of A, achieving effective separation of electrons and holes. The band arrangement of the broken gap (type III) heterojunction (Figure 9c) is similar to that of type II heterojunction. But the CB of semiconductor B is located at an even lower position than the VB of semiconductor A. Thus, under illumination, all carriers (electrons and holes) in semiconductor A cannot be transferred to semiconductor B because the band gaps of A and B do not overlap. As a result, among semiconductor–semiconductor heterojunctions, only staggered gap (type II) heterojunctions are ideal PES cathode materials, and the modulation of electronic structure at the interface of staggered gap heterojunctions (mentioned above) can achieve efficient carrier separation (powered by built-in electric fields), promoting photoelectrochemical energy storage. On the other hand, the band arrangement of the Schottky junction can also effectively promote the separation of charge carriers (photo-generated electrons and holes), thanks to the directional flow of electrons from semiconductor to metal. As shown in Figure 9d, normally, the Schottky heterojunctions are composed of n-type semiconductors and metals, forming rectifying contacts at the interface [119–121]. And in Schottky junctions, the work function of n-type semiconductors is required to be smaller than that of metals. When illumination occurs, the directional charge transfer channel transfers photo-generated electrons from semiconductor to the metal, as well as photo-holes that accumulate on the VB of the semiconductor, ultimately achieving effective separation of charge carriers.

Utilizing the charge separation mechanism of staggered gap (type II) heterojunction, the group of Prof. Wang from the Chinese Academy of Sciences (Fujian Institute of Research on the Structure of Matter) prepared a photo-responsive bifunctional Ni_{12}P_5 @NCNT catalyst for the first time [29]. The heterojunction strongly combines Ni_{12}P_5 nanoparticles and nitrogen-doped carbon nanotubes (NCNT), forming a p-n (type II) heterojunction. In the Ni_{12}P_5 @NCNT heterojunction, p-type Ni_{12}P_5 nanoparticles act as the photo-responsive materials. Thus, under illumination, electrons in the valence band of Ni_{12}P_5 nanoparticles will be excited into its conduction band. Meanwhile, due to the presence of p-n heterojunction interface, photo-generated electrons will rapidly transfer to the conduction band of n-type NCNT, while holes accumulate in the valence band of Ni_{12}P_5 nanoparticles. The generation and effective separation of photo-generated electron–hole pairs are achieved through the redistribution of charges at the heterojunction interface (built-in electric field). Then, photo-generated electrons participate in the ORR process on the NCNT side, while

holes participate in the OER process on the Ni_{12}P_5 nanoparticle side. As a result, the PAZAB with the $\text{Ni}_{12}\text{P}_5/\text{NCNT}$ air cathode demonstrates extremely low charge potential (1.90 V), high discharge potential (1.22 V), and remarkable cycling stability (over 500 cycles), under light irradiation. In addition, all solid-state flexible PAZAB have also been developed and used as power sources to light the commercial LED. This work demonstrates the potential for widespread application of the p-n heterojunction electrode in the fields of portable and wearable electronic devices.

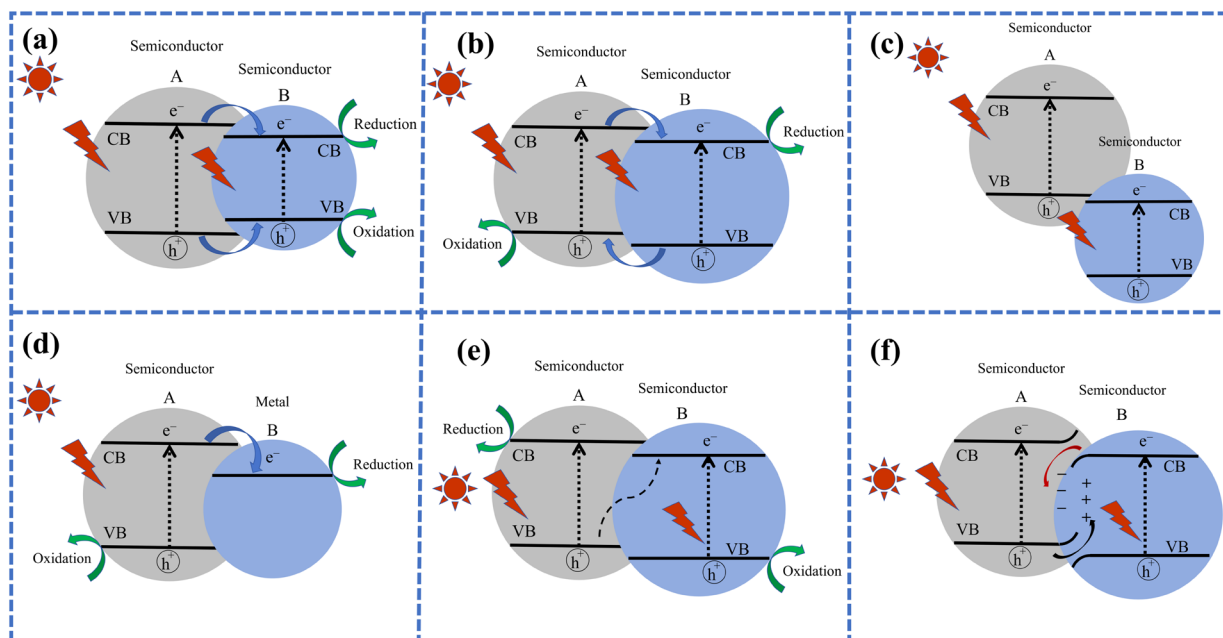


Figure 9. The band arrangement and electronic flow path of (a) straddling gap (type I), (b) staggered gap (type II), (c) broken gap (type III), (d) semiconductor–metal Schottky, (e) direct Z-type, and (f) S-type heterojunctions.

In 2023, a novel Schottky heterojunction photocathode ($2\text{D}/2\text{D Cd-MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$) was manufactured by Liu et al. [122] for photo-assisted Zn–air battery-driven self-powered aptasensor. The Schottky heterojunction photocathode comprises 2D cadmium-doped molybdenum disulfide nanosheets (Cd-MoS_2 NSs) and 2D $\text{Ti}_3\text{C}_2\text{T}_x$ NSs (denoted as $\text{Cd-MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$). Cd-MoS_2 NS is an n-type semiconductor (Figure 10a) and $\text{Ti}_3\text{C}_2\text{T}_x$ NS (one of MXenes) possesses metallic properties [123]; meanwhile, the work function of Cd-MoS_2 (4.82 eV) is larger than $\text{Ti}_3\text{C}_2\text{T}_x$ (4.32 eV Figure 10b). Thus, when Cd-MoS_2 NSs and $\text{Ti}_3\text{C}_2\text{T}_x$ NSs come into close contact, Schottky junctions appear (Figure 10c). At the interface of this Schottky junction, a Schottky barrier and internal built-in electric field are established. Thus, the electron-transfer pathway follows the Schottky heterojunction, transferring from the semiconductors to the metallic materials to achieve thermal equilibrium [124]. Under UV-vis light irradiation, electrons transition from the VB to the CB of Cd-MoS_2 semiconductor due to optical excitation, and then rapidly migrate to the surface of metallic $\text{Ti}_3\text{C}_2\text{T}_x$; meanwhile, holes accumulate in the semiconductor. Therefore, the Schottky junction efficiently separates the photo-generated electron–hole pairs and increases the free carrier concentration, thus promoting the ORR and OER kinetics of PAZABs [125]. Furthermore, the band gap energy (E_g) of $\text{Cd-MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$ is 2.18 eV (Figure 10d), and this appropriate band gap endows the heterojunction photocathode with rapid photo-electron transfer capability from CB of Cd-MoS_2 to $\text{Ti}_3\text{C}_2\text{T}_x$ through the Schottky interface [126]. In addition, the narrow band gap and the Schottky heterojunction interface also improves the visible light absorption capability of $\text{Cd-MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$ photocathode. The $\text{Cd-MoS}_2/\text{Ti}_3\text{C}_2\text{T}_x$

photocathode also has the weakest peak intensity of photoluminescence (PL) among all samples (Figure 10e), corresponding to the least electron–hole recombination and the highest photoelectric conversion efficiency. Thanks to the presence of Schottky heterojunction interfaces, the photo-assisted ZAB displays boosted output voltage, good stability, and wide applicability.

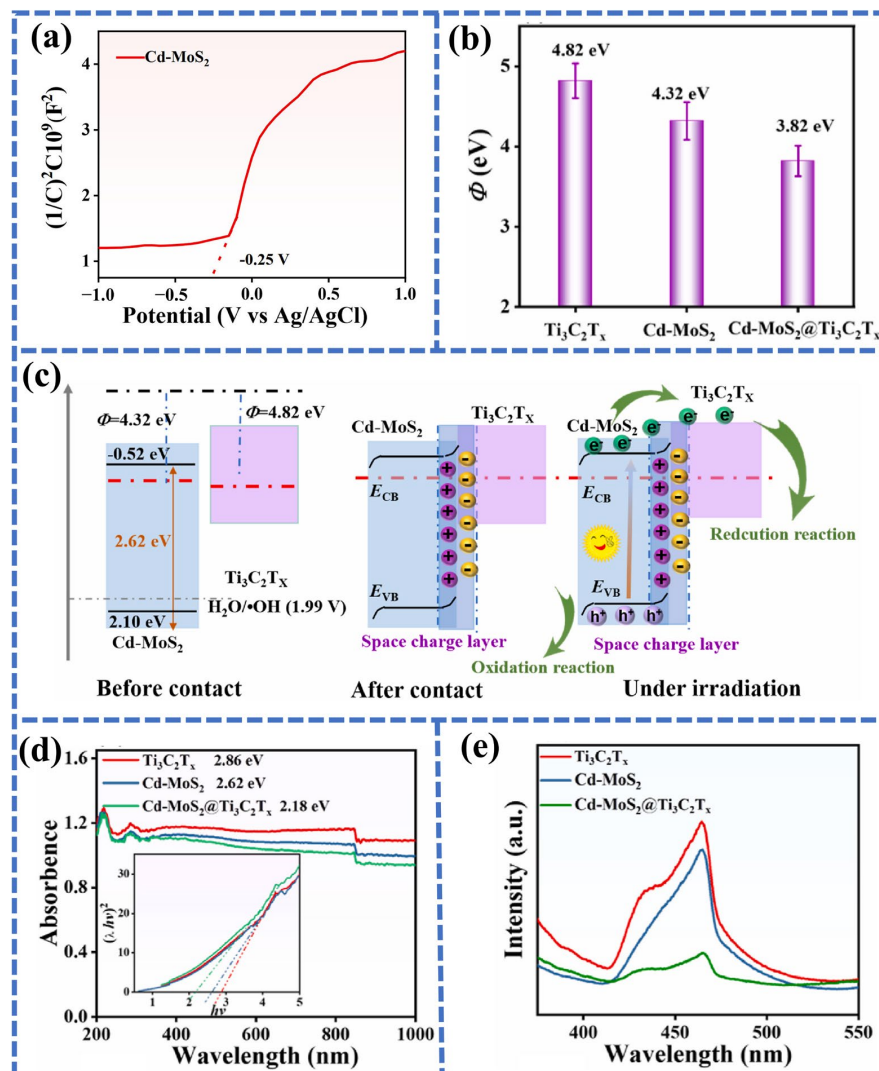


Figure 10. (a) Mott–Schottky curves of Cd-MoS₂. Reproduced with permission [122]. (b) The work function of samples, (c) schematic illustration of heterojunction interface properties under thermal equilibrium and illumination, (d) UV-vis DRS (insert: estimating bandgap through intercept), and (e) comparative PL spectra of samples. Reproduced with permission [122].

In addition, the band alignment of a direct Z-type heterojunction is shown in Figure 9e. This direct Z-type heterojunction is widely used as photocathode catalysts, due to its efficient separation ability of photo-generated electrons and holes, as well as strong redox capability. As we can see, the photo-generated holes in the VB of semiconductor A can directly recombine with photo-generated electrons in the CB of semiconductor B without the need for an electron mediator [127,128]. As shown in Figure 9f, the transfer mechanism of charge carriers in S-type heterojunctions is a combination of the mechanisms in Z-type and type-II heterojunctions. Even more fortunately, S-type heterojunctions can selectively recombine meaningless electrons and holes while retaining effective photo-generated carriers. An S-type C₄N@TiO₂NR heterojunction photoelectrode was developed by Wang et al. [129], which has a staggered band arrangement with a built-in electric field. The unique charge

migration path and superior redox ability endow $\text{C}_4\text{N@TiO}_2\text{NR}$ heterojunction electrodes with outstanding photocurrent response and accelerated oxygen evolution kinetics upon irradiation. Thus, this light and chemical neutralization energy dual-assisted ZAB delivers superior charge/discharge voltages of 0.43/2.02 V and 0.87/1.86 V at 0.1 and 10 mA cm^{-2} , which breaks the limit of conventional ZABs' equilibrium potential (1.65 V).

4.2. Interface Engineering Towards Single-Atom Photocathode

"Interface effects" also exist at single-atom interfaces, and it is expected that interface effects can further enhance the activity of single-atom catalysts (SACs). It is well known that the surface energy of a metal single-atom is extremely high, resulting in serious agglomeration phenomena. The key to successfully preparing durable SACs is to anchor single atoms onto substrates through interface interactions [130]. Research has found that introducing coordination sites can effectively immobilize metal precursors, thereby achieving the atomically dispersed active sites [131,132]. Universally, carbon-supported catalysts containing N-coordinated transition metals (M-N-C) are among the most widely studied SACs in ZABs [3,20–22]. In M-N-C catalysts, nitrogen doping in the carbon substrate facilitates hybridization between the d-orbitals of transition metal atoms and the 2p-orbitals of nitrogen, forming strong transition metal–nitrogen interactions [133]. As a result, isolated atoms can coordinate with nitrogen in dual or quadruple configurations, ultimately forming stable metal- N_2/N_4 -C moieties. The strong interactions in M-N-C ensure stable anchoring of single atoms and robust catalyst structures, making the M-N-C catalysts ideal SACs. Among these, Fe- and Co-based SACs exhibit particularly outstanding performance [22–24]. The interfacial effects in Fe/Co-based M-N-C catalysts fundamentally arise from electronic interactions at the atomic interface, which enhance catalytic activity. In most Fe/Co-based M-N-C catalysts, a Schottky heterojunction forms at the metal-semiconductor interface. Due to the Schottky barrier, electrons unidirectionally flow from the semiconductor to the metal to achieve thermal equilibrium, facilitating efficient charge separation [134,135] (Figure 11a). In ZABs, oxygen can be captured by separated electrons and reduced into O_2^- radicals, while OH^- is captured by holes, promoting the formation of hydroxyl radicals (Figure 11b). This process enhances kinetic performance and enables highly efficient bifunctional catalysis for both the ORR and OER.

In 2022, the research group of Zhang [25] developed an asymmetrically coupled Co single-atom and Co nanoparticle embedded in double-shelled carbon-based nano-boxes (CoNP-CoSA@DSCB). The nitrogen doping in the carbon framework formed Co-N bonding sites, bridging the Co single-atom and Co nanoparticle assembly with the carbon framework, resulting in stable single-atom anchoring and robust structural integrity. In this ideal catalyst, the synergistic effects among components significantly reduce the adsorption/desorption energy barriers of reaction intermediates on the catalyst surface, thereby enhancing both ORR and OER performance. Subsequently in 2024, the team of Zhang [26] designed and prepared S, N co-doped carbon substrate-supported Co single atoms (CoN_4) and S-coordinated Co clusters (SCo_6) as co-catalysts (CoSA-AC@SNC) for ZAB cathodes. This catalyst maintained bifunctional catalytic properties, where Co formed quadruple coordination with N (CoN_4) while S coordinated with Co clusters (SCo_6). The N, S heteroatom doping in the carbon substrate firmly anchored dual Co catalytic sites while modulating the electronic structure of the carbon matrix. The component synergy dramatically enhanced overall catalytic activity, delivering remarkable ORR/OER performance and realizing an ideal Co-based M-N-C bifunctional catalyst.

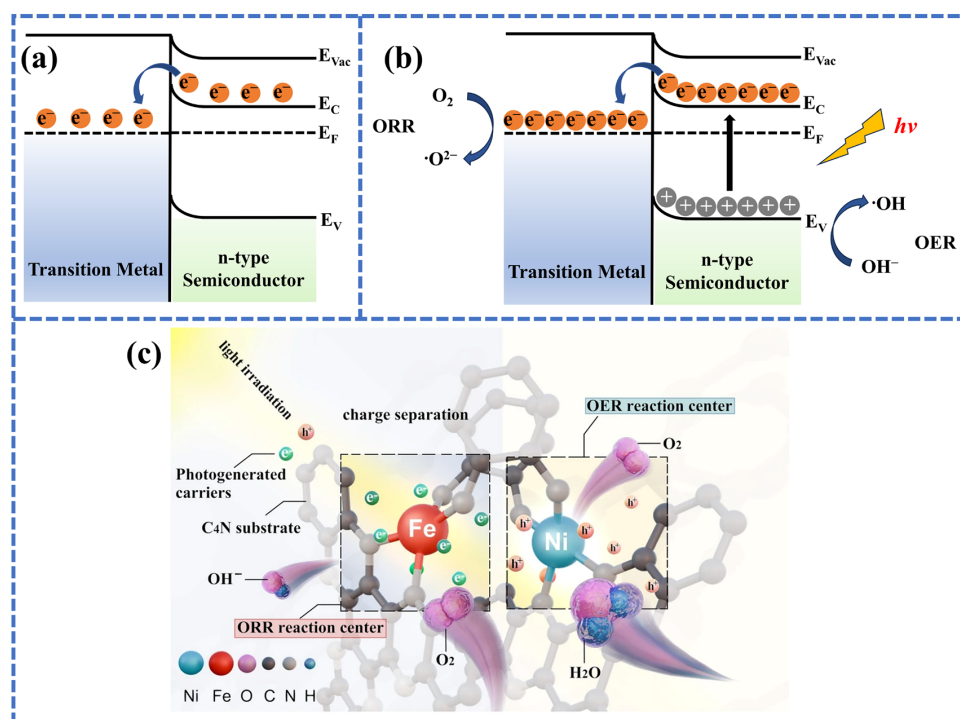


Figure 11. (a) Band structure diagram and electronic flow path of Schottky heterojunction. (b) Separation and transfer of photo-generated carriers under illumination. Electrons transfer to the metal side promoting ORR, while holes remain on the semiconductor side promoting OER. Light illumination promotes charge separation and increases carrier concentration. (c) Schematic diagram of enhanced ORR and OER activity of Janus dual-atom catalyst. Reproduced with permission [136].

Additionally, Professor Zhang [21] et al. recently developed bimetallic ($Co_3S_4/FeS@CoFe/NC$) catalysts, while co-workers of Professor Chen [27] created trimetallic single-atom catalysts ($ZnCoFe-TAC/SNC$). In bimetallic catalysts, $Co-N_x/Fe-N_x$ dual-metal single-atom sites anchored on N-doped carbon nanosheets provided efficient ORR activity, while Co_3S_4/FeS heterojunction particles served as OER catalysts. The cooperation between bimetallic single atoms and nanoparticles optimized intermediate adsorption energy and reaction kinetics through electronic structure modulation [21]. In trimetallic $ZnCoFe-TAC/SNC$ catalysts, Co served as the primary active site for oxygen intermediate binding, Zn sites strongly adsorbed hydroxyl radicals (OH^*) to boost OER activity, while Fe sites downshifted the d-band center of Co to weaken Co-O bonding and enhance catalytic activity [27]. Consequently, these catalysts simultaneously demonstrated outstanding ORR and OER performance. These research advancements not only achieve bifunctional ORR/OER catalysis through the preparation of composite materials but also modulate the interfacial electronic structure by constructing single-atom catalytic sites, optimizing the adsorption energy of reaction intermediates, and simultaneously enhancing reaction kinetics, thereby advancing the development of high-performance ZABs for practical applications.

SACs are also ideal candidates for the photoelectrocatalyst in PAZABs for efficient photoelectrochemical energy storage, which is attributed to their improved optical and electrochemical properties [137–139]. When the photoelectrode uses a single atom as the active site, the single atom serves as the separation center for photo-generated carriers and the donor/acceptor site for electrons [140,141]. Simultaneously, single atoms can reduce the bandgap of photoelectrochemical cathodes and introduce mid-gap defect states. As a result, single-atom catalysts have enhanced light capture ability, suppressed electron–hole recombination, and extended carrier lifetime when used as the air cathode for photo-assisted devices. The unique coordination environments of single atoms endow

the photocathodes with special catalytic active sites and improved electronic conductivity via π -electron modulations, thereby enhancing the electrocatalytic performance of the PES catalysts [142–144]. Specifically, Fe-N₄ and Ni-N₄ sites exhibit outstanding oxygen reduction and oxidation activities, respectively. Liu et al. [136] developed a bifunctional SAC-based photoelectrode, overcoming the challenges of inefficient charge transfer and severe carrier recombination. In their work, a Janus dual-atom catalyst was designed by a one-step hydrothermal strategy. The presence of single atomic sites of Ni and Co can effectively separate photo-generated electrons and holes, making Ni a hole-rich site and Co an electron-rich site (Figure 11c). Therefore, this Janus dual-atom catalyst exhibits enhanced photocurrent, as well as improved catalytic activities of ORR and OER. Furthermore, the Janus dual-atom air cathode shows excellent stability at large current densities in light-assisted rechargeable ZAB. This work presents a clear understanding of the mechanism of a photo-enhanced bifunctional SAC-based air catalyst; meanwhile, it paves the way for the rational design of SAC-based photoelectrocatalysts efficiently converting solar energy into electrochemical energy for storage.

Various advanced characterization techniques are widely used to confirm the dispersed existence of metal single atoms rather than the formation of atomic clusters, such as transmission electron microscopy (STEM), X-ray absorption fine structure (XAFS) measurement, infrared (IR) spectroscopy technique, etc. [17,145–147]. Furthermore, previous research has often obtained complementary results through various tools to comprehensively analyze the properties of SACs. Generally, the morphology, size, and distribution of SACs are elucidated by TEM, and the high-resolution TEM (HR-TEM), selected area electron diffraction (SAED), and aberration-corrected high-angle annular dark field STEM (HAADF-STEM) are often used to determine the monodispersity of metal atoms. The coordination environment and chemical form of single atoms in SACs are widely determined by the X-ray absorption spectroscopy (XAS), and XAS can be divided into three regions: pre-edge region, near-edge region (i.e., XANES), and post-edge region (i.e., EXAFS). Currently, XAFS measurements are essential and crucial approaches to affirm the existent of single atoms, accompanied by XANES originating from the excitation of core electrons to the valence and conduction bands and EXAFS resulting from the scattering interactions of photoelectrons with the neighboring atoms. Fourier-transform infrared (FTIR) spectroscopy is also an effective means of confirming the presence of single atoms, because the way and configuration of the adsorbed CO molecules for the atomic structure are different from that of conventional catalysts. By identifying the specific positions, shapes, and intensities of these CO molecule absorption peaks, the existence of single-atom active sites can be inferred. In situ characterization techniques enable researchers to monitor the dynamic structural and electronic changes in SACs during OER/ORR cycling and under illumination [136,146]. The migration, aggregation, or poisoning of single-atom active sites can be observed in real-time.

For example, Liu et al. [136] revealed the dispersed existence of single atoms through bright spots in HAADF-STEM images, and the elemental mapping revealed the uniform distribution of Fe, Ni single-atom catalytic sites (Figure 12a,b). The appearance of scattering peaks for Fe-N (1.48 Å) and Ni-N (1.5 Å) in XANES reveals the formation of Fe-N and Ni-N bonding, whereas the absence of metal–metal scattering path indicates the atomic dispersion of Fe and Ni atoms (Figure 12c). The coordination numbers of single atoms in the Janus dual-atom catalyst (JDAC) sample are estimated by the EXAF, and the coordination numbers of Fe and Ni atoms are 3.80 and 4.22, respectively (Figure 12d,e), verifying the formation of Fe-N₄ and Ni-N₄. The results of wavelet transform (WT)-EXAFS of the k₂-weighted EXAFS for Fe and Ni atoms further show the presence of Fe-N and Ni-N bonds; nevertheless, the absence of metal bond signals confirms that the metal elements are mainly

distributed as single atoms with metal-N₄ paths, instead of aggregating into metal clusters or nanoparticles with metal-metal bonds. Moreover, in situ XANES analysis is performed to investigate the single-atom sites during the OER and ORR cycling. Under illumination, the absorption edge of Ni exhibits a rightward shift (Figure 12f), and the absorption edge of Fe exhibits a leftward shift (Figure 12g), indicating the increases and decreases in oxidation states, which are attributed to enrichments of photo-generated holes on Ni atoms and photo-generated electrons on Fe atoms, respectively. As a result, Ni and Fe atoms form photo-generated hole and electron enrichment centers, greatly enhancing the OER and ORR catalytic activities of JDAC. In addition, under light illumination, the interaction between Ni and H₂O, as well as Fe and O₂, are investigated. The results indicate that OER-adsorbed reactant OH[−] is more likely to occur at the Ni site with a higher hole density (Figure 12h,j) in the presence of H₂O, and the bond is more likely to form between Fe and O₂ in the presence of O₂ (Figure 12i,k), under light illumination. By conducting ex and in situ XANES analysis, the existence and stability of single-atom sites have been verified, and the underlying mechanisms of enhanced ORR/OER processes have also been revealed. Briefly, ex situ and in situ XAFS technologies may be the most reliable and insightful characterization techniques used to confirm and dynamically monitor the stability of single atoms in SACs. And the in situ XAFS can also elucidate the operational mechanism of the photo-enhanced Zn–air battery.

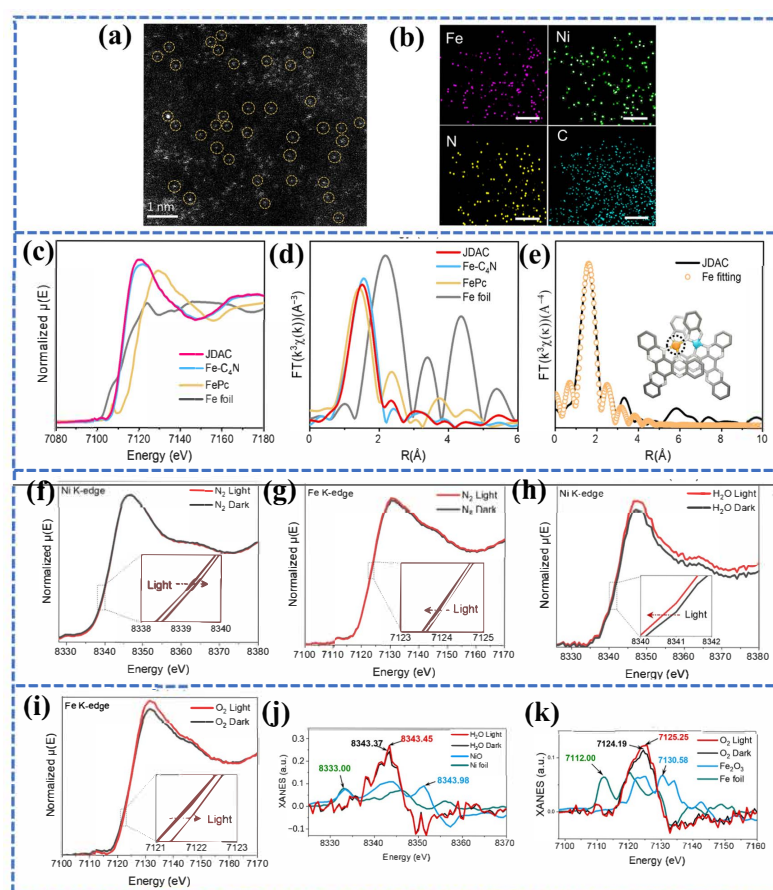


Figure 12. (a) HAADF-STEM image of Janus dual-atom catalyst and single atoms are marked with circles. (b) EDS elemental mapping of sample. (c) XANES spectra of Fe K-edge. (d) Fourier transformation-EXAFS and (e) EXAFS fitting curves of Fe (insert: demonstrating a stable four-nitrogen coordination structure of Fe and Ni). In situ K-edge XANES of (f) Ni and (g) Fe with and without illumination in N₂. In situ XANES of (h) Ni K-edge in H₂O and (i) Fe K-edge in O₂ with and without illumination. The first-derivate XANES plots of (j) Ni K-edge and (k) Fe K-edge. Reproduced with permission [136].

5. Summary and Prospects

The features of PES devices and types of PES materials are elaborately summarized in this review. In particular, the development of PAZABs with the advantages of high efficiency and low cost is systematically summarized in terms of the working principles, types of photocatalytic air cathode materials, and electrochemical performances. A dual functional photoactive electrode is the key component of a photo-assisted ZAB, which can directly convert solar energy into electrochemical energy. Normally, photoelectrochemical energy storage of heterojunction materials proceeds through two steps: firstly, the air cathode needs to absorb solar energy and generate carriers (hole–electron pairs); then, such charges take part in charge/discharge processes, thereby transferring the energy to the electrochemical energy storage materials. “Interface effects” promote the transfer of photo-generated carriers and suppress the recombination of electron–hole pairs, thereby achieving efficient separation of charges, enhancing the ORR and OER activity of heterogeneous air catalysts.

Although many studies have investigated the electrochemical performances of PAZABs and explored the possibility of their practical application by preparing flexible all-solid-state photo-assisted batteries, the commercialization of PAZABs replacing lithium-ion batteries still faces several bottlenecks: 1. The emergence of photo-generated electrons/holes in the photo-response air cathode is key to improving the kinetics of ORR and OER processes. However, the electrolyte and impurities in the battery will consume electrons/holes, thereby reducing the utilization efficiency of solar energy and the stability of the device. 2. The limited lifetime of photo-generated carriers severely confines the storage of electrochemical energy. Only when the electrode material is thin enough, can the diffusion path of charge carriers be shortened to meet the separation of short-lifetime carriers. However, the thin PES materials represent a low mass loading of active materials, which will reduce the energy storage capacity of the battery. 3. The detailed mechanisms of PES processes are still not revealed. The absence of detailed mechanisms will hinder the research and development of ideal materials and devices. 4. The dendrite issues are commonly present in metal air batteries. In liquid battery systems, the formation of dendrites can cause short circuits in cells, thereby increasing the risk of self-ignition of batteries. How to avoid the formation of dendrites and reduce the impact of dendrites is crucial for the practical application of PAZABs. 5. Some metrics are very important for the evaluation of PAZABs, such as incident photon-electron conversion efficiency (IPCE) and solar-to-electrochemical (STEC) efficiency, but many research works lack these metrics.

Facing the aforementioned challenges, we put forward several prospects and suggestions for the further development of PAZABs: 1. The arrangement of energy bands is crucial for achieving carrier separation and improving the photocurrent, as well as enhancing the reaction kinetics of ORR and OER. Therefore, theoretical analysis and simulation calculations play an important guiding role in the development of PES devices. 2. Detailed material characterization is of great significance for photocatalytic cathode design and PES device exploitation. Introducing in situ characterization into the study of photoelectrochemical properties of PES materials is beneficial for revealing the deep mechanisms of solar energy conversion and chemical energy storage. 3. Due to the early stage of device research in the scientific community, standard battery configurations and testing protocols have not yet been established, making peer review difficult to conduct. Therefore, a unified PAZAB evaluation standard based on a benchmark PES material needs to be established as soon as possible.

Overall, against the backdrop of increasingly severe environmental pollution and the gradual depletion of fossil fuels, we believe that amongst direct solar electrochemical energy storage devices, PAZABs using PES materials as air cathodes are expected to become

an ideal next-generation energy solution. Meanwhile, to achieve this goal, researchers still need to invest more efforts in the rational design of photocatalytic cathode materials and the study of their underlying working mechanisms.

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