Photoactive nanomaterials enabled integrated photo-rechargeable batteries

Abstract: The research interest in energy storage systems (e.g., batteries and capacitors) has been increasing over the last years. The rising need for electricity storage and overcoming the intermittent nature of renewable energy sources have been potent drivers of this increase. Solar energy is the most abundant renewable energy source. Thus, the combination of photovoltaic devices with energy storing systems has been pursued as a novel approach in applications such as electric vehicles and smart grids. Among all the possible configurations, the “direct” incorporation of photoactive materials in the storing devices is most attractive because it will enhance efficiency and reduce volume/weight compared to conventional systems comprised two individual devices. By generating and storing electricity in a singular device, integrated photo-rechargeable batteries offer a promising solution by directly storing electricity generated by sunlight during the day and reversibly releasing it at night time. They hold a sizable potential for future commercialization. This review highlights cutting-edge photoactive nanomaterials serving as photoelectrodes in integrated photobatteries. The importance and influence of their structure and morphology and relevant photocatalytic mechanisms will be focal points, being strong influencers of device performance. Different architecture designs and working principles are also included. Finally, challenges and limitations are discussed with the aim of providing an outlook for further improving the performance of integrated devices. We hope this up-to-date, in-depth review will act as a guide and attract more researchers to this new, challenging field, which has a bright application prospect.

Keywords: energy storage systems; morphology; nanomaterials; photoactive materials; photobatteries; photocatalysis.

1 Introduction

The development of human society is causing an unprecedented increase in energy demand [1]. The limited supply of fossil fuels and the increasingly serious environmental pollution have become major global problems. In order to address these issues, it has become crucial for the scientific community to explore sustainable energy sources, including hydroelectric power [2], wind [3], solar [4–6], ocean [7], geothermal [8], and biomass [9] energy. Because of its unlimited nature and sustainability, solar energy is recognized as the most promising and economic alternative to traditional fossil fuels [10, 11]. The use of solar cells as an energy conversion technology can effectively meet our long-term needs [12, 13]. However, this process is dependent on the availability of energy sources and is not always in alignment with actual demand [14, 15]. Several solar energy conversion and storage devices have been proposed as solutions. These include rechargeable (secondary) batteries (e.g., lithium-ion, lithium–oxygen, lithium–sulfur batteries, zinc-ion, redox flow batteries, etc.) [16–20] and supercapacitors [21–23] coupled with a solar cell [24–27]. Some of these devices are currently being used in a variety of fields such as electrical vehicles and portable electronic devices, among others [28, 29].

One obvious solution lies in the combination of a photovoltaic cell (silicon, dye-sensitized or perovskite solar cells) with an external electrochemical device (e.g., rechargeable battery or capacitor). The former acts as an energy harvester whereas the latter stores electricity externally in the form of chemical energy. These two individual systems are linked via external wire connection.
However, they suffer from increased Ohmic resistance, energy mismatch, and low levels of integration between the two systems, which leads to bulky, inflexible devices and high energy losses [30, 32, 33].

An attractive alternative to devices relying on discrete modules and external wires connection is an integrated photo-rechargeable energy storage system [34–37]. Photobatteries (PBATs) [31, 37, 38], photocapacitors (PCAPs) [36, 39–41], and redox flow batteries (RFBs) [42–44] are included in this category. The advantages of integrated systems are their flexibility, light weight, high safety and smaller volume compared to the wired systems [30, 45]. They can be readily implemented in wearable electronics, implanted biosensors and smart optoelectronics, widening the application fields [46–48]. However, these devices do not allow practical applications due to their low performance to date.

The most commonly used batteries are based on a metal anode, with lithium, zinc, and sodium being the most representative examples of anode materials. Among them, lithium-based materials are most studied and used as anode nowadays in solar rechargeable batteries [14, 37, 45, 49]. The major advantage of using lithium is its large theoretical energy density (3560 W h kg⁻¹) [50]. In addition, because of its small size, lithium ions can easily intercalate into other nanomaterials with a high insertion/removal rate, without modifying their structure (i.e. MnO₂) [51]. However, Li-based PBATs present a major drawback related with the significantly large overpotential (4–4.5 V) during the charge process, which leads to high voltage gaps and low round-trip efficiencies [52–54]. Particularly, the degradation of Li–O₂ PBATs is linked to the incomplete dissolution of Li₂O₂ even at high voltages and the accumulation of parasitic products in the cathode, which ultimately causes decaying in the overall capacity over cycles [55, 56]. Zinc has high specific capacity (820 mA h g⁻¹ and 5854 mA h cm⁻²), good stability in aqueous electrolytes, low toxicity, high safety, low cost, and it is environmentally friendly [57–59]. With these properties, it has the potential to become the new energy storage material. In general, metal-based PBATs suffer from slow intrinsic diffusion of metal ions in a solid material, which limits the intercalation rate, and from sluggish reaction kinetics towards oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Because of these problems, the focus should be on finding a photoactive bifunctional material towards OER and ORR that can also improve the light harvesting capability, reduce charge recombination, increase the surface area to enhance a better contact with the electrolyte and allow a higher metal ion insertion/removal rate [60, 61]. Nanomaterials are a promising solution that offers all the above mentioned qualities [62–64]. Vanadium oxides with nanowires or nanorods morphology have been proven to be the best candidates to be used as PEs. J. Wang et al., reported a photo-rechargeable lithium-ion battery using LiV₂O₅ as a photocathode with a photo-to-electric conversion efficiency of 9%, the highest value published to date [65]. Other devices based on V₂O₅ nanofibers obtained photo-to-electric conversion efficiencies of 2.6% [66] and 1.2% [59] in Zn–air and Li-ion PBATs, respectively. Other nanomaterials that form 2D nanosheets (such as siloxene, SiC and g-C₃N₄) have shown high capacities [67–69]. However, there still remain many challenges to overcome in order to improve the device performance. Low light absorption, high charge recombination, poor charge transport capabilities, and low photo and chemical stability are the major drawbacks preventing higher battery efficiencies. In addition, sluggish kinetics between the nanomaterial and the redox active species in the electrolyte limit their photocatalytic performance [70–72]. Great efforts are being made to fabricate cost-effective devices with high energy conversion efficiency and good compatibility between the photo-conversion and energy storage components [73].

As seen in Figure 1, the number of publications dealing with integrated photo-rechargeable batteries and photocapacitors has raised exponentially over the last ten years, thanks to the great efforts of many investigators, who have devoted to exploring different strategies, materials and processes in order to achieve highly efficient devices and understand the underlying mechanisms [44, 74].

![Figure 1: Annual publication number on integrated photobatteries (red) and photocapacitors (blue). Data were retrieved from Web of Science on November 09th, 2021, by searching "TS = (solar rechargeable bat* or photo-assisted bat*)" and "TS = (photocapac* or photosupercapac* or photo integrated supercapac*)".](image-url)
accumulated knowledge now enables us to better realize the rational design, which is the key to the rapid development of more efficient energy storage systems. Some excellent reviews dealing with photobatteries from a device performance perspective have been published [14, 38, 43–45, 75, 76]. However, an up-to-date report of the most relevant photo-active nanomaterials used in photobatteries, from a structural and morphological point of view, has not been done yet.

This review first introduces major configurations and working principles in addition to basic concepts in electrochemistry and energy storage. It is followed by a summary of photo-active nanomaterials incorporated in the photoelectrode (PE), emphasizing the influence of their structure and morphology in the energy harvesting and storing. The most notable photocatalytic mechanisms that govern light-to-electricity energy conversion are also included. Ultimately, a discussion of the challenges and limitations of photoelectrodes in integrated systems is presented along with ideas for rationally designing bifunctional photo-active nanomaterials that serve as photoelectrodes.

2 Architecture design, working principles, and basic concepts in photobatteries

Previous reports in the field classify integrated photobatteries according to the number of electrodes (two or three), the physical state of the active materials (solid, liquid, and gas) or the anode materials (e.g., lithium, zinc, and sodium). Here, we describe the photobatteries based on the nature of the photoactive material in the PE. This is a novel point of view that will promote future rational design of PEs in solar-rechargeable batteries. Prior to that, we briefly introduce the different types of configurations, outlining working principles and basic concepts to create a foundation before addressing the topic of interest for this review.

The first photo-rechargeable battery was reported by Hodes and co-workers in 1976, where they described a three-electrode system composed of cadmium selenide/sulfur/silver sulfide (CdSe/S/Ag2S) [77]. Since then, several reports have been published on the same material exploring different hybrid photoelectrodes, such as silicon/silicon oxide, dye-sensitized titania (TiO2)/poly/3,4-ethylenedioxythiophene, (PEDOT) [78] and dye-sensitized TiO2 nanorods [79] (Figure 2A). They usually consist of a photoelectrode (PE), a counter electrode (CE) that works as a redox electron transfer surface, and an energy storage electrode. Under illumination, the photo-active material in the PE creates electron–hole pairs. If the voltage generated is sufficient to activate the electrochemical charging process inside the battery, the electrons travel to the anode where they are either stored or used to reduce the active species. Meanwhile, holes in the PE are counterbalanced by electrons at the CE or by redox species that will be reduced at the CE [45, 76]. If the voltage is insufficient to reduce the active species, an external bias must be applied. In these cases, we say that the device is a photo-assisted rechargeable battery. It helps to reduce the overpotential, but these devices cannot be charged solely with solar energy.

On the other hand, two-electrode integrated PBATs allow direct conversion and storage of the solar energy without any additional energy source [30, 80]. They consist of a photoanode and a photocathode where one or both can contribute to energy conversion as well as to energy storage [35, 74, 76]. Under illumination, the photoactive material in the PE (a semiconductor) generates photoexcited carriers (electrons and holes) through the photovoltaic effect. They interact with redox-active species from the energy storing electrode and reduce them with or without external electrical bias [38, 49]. The holes can oxidize other redox active species or be engaged in OERs. A schematic diagram of two and three photo-assisted rechargeable battery configurations are shown in Figure 2A and B.

In the 1980s, we can find the first publications reporting two-electrode configurations. For example, Sharon et al. developed a two-redox-electrolyte system divided into two compartments based on BaTiO3|Ce4+/3+|Fe3+/2+|Pt. Ce4+ was oxidized to Ce4+ on the surface of the PE and Fe3+ reduced to Fe2+ on the counter electrode in the photocharging process [81]. Other examples of two-electrode integrated systems are reported in more recent publications such as the one by Wang et al. in 2015, where they reported a photo-assisted rechargeable battery based on a dye-sensitized solar cell (DSSC) with a lead-organohalide electrolyte (CH3NH3I·PbCl2). In this case, Pb2+ is reduced into Pb at the interface of dye–TiO2 PE with photogenerated electrons from the dye. Meanwhile, Pb2+ is oxidized into PbO2 at the Pt counter electrode during charging step (Figure 2C). During the discharge, electrons return to the Pt electrode from the dye–TiO2 PE when Pb is oxidized to Pb4+. The overall reactions of charging and discharging are summarized in Eq. (1) [82]. Paolella et al. introduced a two-electrode system involving direct photo-oxidation of lithium iron phosphate (LiFePO4; LPF) nanocrystals in the presence of dye N719 at the photocathode. Figure 2D shows the photocharging mechanism. Photogenerated holes in the dye aid the delithiation of LFP and photogenerated electrons reduce oxygen (O2) into peroxide and/or superoxide species that will react with the
Figure 2: Battery configuration of integrated (A) three-electrode PBAT, (B) two-electrode PBAT [51]. Copyright 2020, John Wiley and Sons; (C) Redox reactions at the electrodes under charging and discharging processes [82]. Copyright 2015, John Wiley and Sons; (D) Global photo-assisted charging mechanism of Li-ion PABT [83]. Copyright 2017, Springer Nature; (E) Energy diagrams for the discharge and charge voltage under illumination; (F) reactions in discharge and charge processes [84]. Copyright 2019, John Wiley and Sons; SFB with (G) single photo-electrode (H) dual photoelectrodes [44]. Copyright 2018, John Wiley and Sons.
carbonate-based electrolyte. Li electrode enabled favourable nucleation sites for the formation of a solid electrolyte interface (SEI) formed by Li-carbonate-based compounds (ROOLi) [83]. In this case, no external current is applied between the electrodes during illumination and contrary to what it is expected in a regular Li-ion PBAT, lithium is not reduced and deposited on the lithium anode. During discharge, SEI crystals partially dissolved, releasing Li⁺ ions that travel to the cathode to form LPF (see Eqs. (2) and (3)). In 2019, Zhuo et al. reported an aprotic Li–O₂ PBAT using C₃N₄ as a photocatalyst in the photocathode [84]. The photochemical mechanism is explained in Figure 2E and F. During charge, C₃N₄ captures light, leading to photogenerated electrons and holes at the conduction band and valence band, respectively. Holes promote the decomposition of Li₂O₂ into Li⁺, which will be reduced to Li at the anode by the photogenerated electrons (see Eqs. (4) and (5)). Therefore, the charging voltage is reduced up to 3.38 V. During discharge, O₂ is reduced to O₂⁻ and O₂²⁻ in the cathode followed by its reaction with Li⁺ ions present in the electrolyte to form Li₂O₂ (Figure 2F). The value of discharge voltage under illumination (3.22 V) is related to the energy difference between C₃N₄ valence band and Li⁺/Li redox potential, and it is higher than that of the equilibrium (2.96 V), indicating the beneficial conversion of solar energy into electricity. Likewise, the charge voltage is greatly reduced (from 4.09 to 3.38 V) in the presence of light.

\[
2\text{Pb}^{2+} (aq) + 2\text{H}_2\text{O} (aq) \xrightarrow{\text{ds}} \text{PbO}_2(s) + \text{Pb}(s) + 4\text{H}^+ (aq) \quad (1)
\]

\[
\text{LiFePO}_4 + \text{dye}^* + \text{O}_2 \rightarrow \text{FePO}_4 + \text{Li}^+ + \text{dye} + \text{O}_2 \quad (2)
\]

\[
\text{FePO}_4 + \text{e}^- + \text{Li}^+ \rightarrow \text{LiFePO}_4 \quad (3)
\]

\[
\text{Li}^+ + \text{e}^- (\text{C}_3\text{N}_4) \rightarrow \text{Li} (\text{anode}) \quad (4)
\]

\[
\text{Li}_2\text{O}_2 + \text{h}^+ (\text{C}_3\text{N}_4) \rightarrow 2\text{Li}^+ + \text{O}_2 \quad (5)
\]

A general idea of the mechanism of a PBAT has been described as well as some relevant examples. However, due to the complexity of the systems, especially the differences on the PE materials and device architecture, the mechanism of each system should be studied individually. The photoactive material at the PE plays a key role in the PBAT mechanism. Its structure, morphology, energy levels and the reaction kinetics between the redox active species and the photogenerated electrons and holes at the PE will highly influence the performance and stability of the PBAT. For instance, BiVO₄ (BVO) PE has been studied and compared to Fe₂O₃ PE to assess the effect of the band structure on LiO₂ and Zn–air PBATs [85, 86]. BVO presented severe photocorrosion and lost its photocatalytic activity soon after starting photocharging. Under the same conditions, Fe₂O₃ PE showed high stability over up to 41 cycles.

RFBs store electrical energy via two liquid redox-couple electrolytes called anolyte and catholyte. The electrolytes are separated by an ion-selective membrane and can be stored in external reservoirs of different volumes. This allows scaling up the energy storage capacity by using larger electrolyte tanks. Due to direct electrode contact with the liquid electrolyte, the working temperature is lower compared to its “solid” counterparts, which grants RFBs higher stability and durability [42, 43, 87, 88]. This is extremely important in solar integrated devices since exposure to sunlight will raise solution temperature, which is deleterious for optimal battery functioning. Integrated solar flow batteries (SFBs) combine a solar energy conversion system with a rechargeable RFB. One or two PEs enable the photocharging process. The working principles are very similar to those found in two and three-electrode systems. In the PE, the generated electron–hole pairs interact with the anolyte, converting the solar energy into chemical energy that will be stored directly in the tanks (see Figure 2G and H). Holes diffuse to the cathode and oxidize the catholyte while electrons move to the anode and reduce the anolyte. The internal charge is balanced by ion species that travel through the membrane or separator [44, 74]. The first publication integrating a photovoltaic system (DSSCs) with nonaqueous redox couples obtained currents of 0.1 mA/cm² and efficiencies lower than 0.1% [89, 90]. Since that time, solar-to-output electric efficiencies up to 20.1% [91–93] have been achieved through fabrication of single-junction silicon photodelectodes, perovskite/silicon tandem solar cells, or single-junction GaAs photoanode.

The overall energy efficiency is an important parameter of any integrated energy conversion and storage device, including rechargeable battery systems and directly reflect how effectively the device can convert one type of energy to another (typically between electric to chemical energy). Specifically, for solar rechargeable batteries, there are three main processes that determine the overall energy efficiency: solar-to-electric energy conversion, electric-to-chemical energy conversion (photocharging step) and reversible chemical-to-electric energy conversion (discharge step). The electric-to-chemical energy conversion is the stage that limits overall efficiency. The following formula can be used to define photo-electric conversion efficiency (η_conversion):

\[
\eta_{\text{conversion}} = \frac{E_{\text{output}} (\text{battery discharging})}{E_{\text{input}} (\text{solary energy})} = \frac{E_A A_1}{P_m A_1} \quad (6)
\]

where \(E_{\text{output}} (\text{battery discharging})\) and \(E_{\text{input}} (\text{solary energy})\) represent the discharging energy of the battery and the solar energy applied during charging, respectively. \(E_A, A_1, P_m,\)
$t$, $A_2$ correspond to the areal energy density, the surface area of the PBAT, the light intensity, the photocharging time and the illuminated surface area [59, 83, 94].

Another highly cited concept is the round-trip efficiency or energy efficiency ($\eta_{\text{battery}}$) that is used in photo and non-photo rechargeable batteries. It is the relationship between the output electric energy $E_{\text{output}}$ and the input electric energy $E_{\text{input}}$, dependant on the charging and discharging rate [95, 96]. Equation (8) displays Coulombic efficiency (CE). It is the proportion between the capacity during discharge (total charge extracted from the battery) and charge (total charge put into the battery over a full cycle) [97, 98]. In the same way, voltage efficiency ($V_{\text{eff}}$) in Eq. (9) corresponds to the ratio between the discharge voltage and the charge voltage, either in the dark or under illumination.

$$\eta_{\text{battery}} = \frac{E_{\text{output}}}{E_{\text{input}}} \quad (7)$$

$$CE = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} \quad (8)$$

$$V_{\text{eff}} = \frac{V_{\text{discharge}}}{V_{\text{charge}}} \quad (9)$$

### 3. Photoactive nanomaterials working as bifunctional photoelectrodes

PE is one of the key factors in the development of high-performance photobatteries and usually sets the limit of the overall efficiency. Therefore, the design and selection of the materials, composites or heterojunctions that comprise it are essential for efficient conversion and storage of the solar energy [31]. As we previously mentioned, the PE consists of either a simple semiconductor or a photovoltaic cell. In the latter, the PE is part of the energy conversion unit and works independently from the storage system. In this case, it needs to meet the specific requirements for an efficient solar cell. Integrated devices composed of a solar cell that shares an electrode with the battery component are outside the scope of this review. Many publications have already dealt with this topic, including silicon solar cells [93, 99, 100], DSSCs [101–106], perovskite solar cells (PSCs) [107–110], and other 3-electrode systems [111] coupled with a regular rechargeable battery. The mechanisms underlying solar and battery systems can also be found elsewhere [31, 45, 112]. In integrated two-electrode photobatteries, we refer to the PE as bifunctional because it must accomplish two purposes: harvest energy from sun light and store it chemically. To ensure light absorption in a wide range of the spectrum, the optimal bandgap of the semiconductor should fall between 1 and 2 eV [113]. In addition, the PE should be photo-, thermo-, and chemically stable within the working voltage range during charge and discharge. This is a critical factor that greatly influences the lifetime of the battery.

Batteries can store energy via two processes: redox reactions and/or ionic transfer electrolytes. Both mechanisms need an efficient charge transport between the PE and the electrolyte. An efficient charge carrier transport is not only conditioned by the energy levels, but also by the morphology, defect concentration and doping level of the semiconductor material in the PE [113]. Additionally, it is desirable that the nanomaterial offers a high specific surface area providing extensive contact with the electrolyte. If the working mechanism involves the insertion of metal ions (Li⁺, Na⁺, K⁺), it should have interstitial sites to reversibly accommodate these ions without deforming or cracking the nanostructure [114].

Finally, the requirements for the band-edge positions vary depending on the type of batteries. For intercalation photobatteries, there should be a trade-off between the CB position of the photoactive semiconductor and the redox reaction to compensate the charge imbalance due to cation intercalation [113]. In the case of Li–O₂ photobatteries, the redox potential of O₂/Li₂O₂ couple must be positioned between the VB and CB of the semiconductor [84, 115]. On the other hand, RFBs batteries have a more complex system with different redox active species. The electron acceptor redox level should be lower than that of the semiconductor’s CB and the VB of the semiconductor should be placed lower than the electron donor level [116]. However, the VB cannot be too positive in order to avoid solvent oxidation on the PE surface. Consequently, a deep study of the band alignment between the photoactive material and the active redox couples has to be carried out to maximize the storage performance, stability and ensure an optimal thermodynamic compatibility in the integrated system [75].

Although there are many articles describing rechargeable batteries, such as Li-ion batteries, Li-ion [111], Li–O₂ batteries [117, 118], Li–S batteries [109, 119], non-Li anode–air batteries [73, 120] and metal photo-intercalation batteries [113], based on the working electrode composition, which are built on different working principles and also review articles focusing on nanomaterials in non-photo rechargeable batteries, there is no publications concerning photoactive nanomaterials for solar rechargeable batteries. Considering the importance of the PE material in integrated solar-batteries, the review is organized by PE composition,
rather than battery configurations or types as shown in previously published review articles.

We focus on nanostructured materials because of the unique characteristics arising from their nanometer size. Compared to bulk materials, lower dimensional (2-, 1-, 0-dimensional: 2D, 1D, 0D) nanomaterials tend to have a more uniform size distribution, which enables the control of their properties. Their higher surface area allows larger contact area with the electrolyte, thus, higher ion flux across the interface [121, 122]. As a result, the rate and the kinetics of ion insertion/removal are enhanced in intercalation batteries. Additionally, they facilitate reactions that cannot occur by materials composed of micrometer-sized particles. For instance, reversible ion intercalation can take place in the mesoporous nanostructure of $\beta$-MnO$_2$ without any structure destruction [51]. Another advantage is that in some cases, due to the orientation of the nanostructures (e.g. nanowire arrays) the charge transfer is favored in one specific direction, reducing charge recombination. It also tends to be easier to tune the bandgap and electronic band structure of nanomaterials by modifying their size, doping, etc. [123]. Nanomaterials usually work throughout photocatalytic reactions that benefit from aforementioned high specific surface areas, optimal interfacial charge transfer and high porosity [124, 125]. However, it may be noted that their large surface area could lead to a large number of side reactions with the electrolyte and the synthesis of a particular nanostructure could be relatively complex to achieve [60]. In the following section, a description of state-of-the-art nanomaterials employed in solar rechargeable batteries is presented.

### 3.1 Dye-sensitized photoelectrodes

The idea behind dye-sensitized photoelectrodes stems from DSSCs, where an organic dye is commonly attached to a layer of mesoporous TiO$_2$ (or an alternative wide bandgap oxide) with a ~20 μm particle size. The film is commonly deposited by doctor blading or screen-printing techniques and its thickness is usually 5–20 μm [24, 126]. When light strikes the dye, the photogenerated electrons are transferred to the CB of TiO$_2$ and the holes are quenched by electrons coming from the electrolyte. Frequently, this is an organic solvent containing a redox system such as iodide/triiodide ($I^-/I_3^-$). Desirable morphologies of TiO$_2$ films have mesoporous channels or nanorod nanostructure aligned in parallel to each other, but perpendicular to the contact or charge collector [127, 128]. A thin dense blocking layer of TiO$_2$ is also often deposited between the mesoporous layer and the charge collector to prevent direct contact between the later and the electrolyte [24, 126, 129, 130]. The advantages of this morphology include a high surface area for sensitizer adsorption, favorable electron transport and enhanced light-scattering by metal oxide [127]. All these together contribute to increased light absorption of (and thereby charge generation in) the dye sensitizer and charge carrier separation. Because the dye is mainly responsible for light absorption in this system, it is desirable to have one, whose absorption covers a wide wavelength range in the visible regime and even extends to the near-infrared (NIR) part. Similarly important, considering the device lifetime, the dye should be electrochemically and thermally stable and also have a strong binding with the metal oxide. In the case of the strongest interfacial interaction, the dye is covalently bound to the semiconductor surface. It must thus contain anchoring groups (i.e. −COOH, −SO$_3$H). The energy levels should allow for electron transfer to TiO$_2$ and regeneration by the electrolyte [126, 130]. The photoelectric conversion remains as the key factor that determines the overall efficiency of the device [30]. Several publications have used this DSSCs approach [90, 105, 131].

One example is the report of McCulloch et al. where the PE is formed by TiO$_2$ sensitized with ruthenium-based Z907 dye in an SFB [132]. They achieved Coulombic efficiencies up to 91% over 50 cycles along with a high range of pH. In 2017, Paolella et al. published triphylite (LiFePO$_4$, LFP) nanoparticles (NPs) sensitized with N719 dye in Li-ion batteries [83]. LFP showed complete delithiation by the photo-holes produced in the dye when illuminated, leading to the formation of heterosite (FePO$_4$). High-resolution transmission electron spectroscopy (HRTEM) found that the lattice constant of LFP decreased from 0.296 nm to 0.289, confirming the reduced volume of the de-lithiated FePO$_4$ structure (see Figure 3A and B). The photo-oxidation and overall efficiency were promoted by ball-milling LFP, which greatly increased the surface area, facilitating the charge transfer between the dye and LFP nanoplatelets. Despite a relatively low photon-to-electric efficiency of 0.06–0.08%, this pioneering work revealed that photogenerated charges can be stored chemically as a solid electrolyte interphase (SEI) layer at the Li metal electrode (as it happens in a classic Li-ion battery, where Li$^+$ ions are deduced to Li metal) but without the help of an external circuit [37]. The low current efficiency was attributed to large charge recombination losses at the LFP/dye/electrolyte interface. Since the dye cannot store the photogenerated charge, Xu et al. designed a composite formed by TiO$_2$/N719 dye/Cu$_2$S to act as photocathode in a solar rechargeable Li–S battery [133]. By depositing Cu$_2$S on top of the dye, the third electrode is no longer needed, creating a bifunctional PE that can harvest light and store it.
first discharge step, Cu$_2$S is reduced to Cu(0) and Li$_2$S is formed. During photocharging, the dye has the same function as in a regular PBAT, but instead of being regenerated by the electrolyte, the photogenerated holes oxidize Cu/Li$_2$S into Cu$_{1.96}$S/Li$^{+}$ while electrons reduce Li$^+$ to Li metal at the anode. The following discharge steps consist of the reduction of Cu$_{1.96}$S/Li$^{+}$ into Cu/Li$_2$S. The oxidation reaction between the dye$'$ and Cu$_2$S is expected to be more efficient and stable compared to that of dye$'$ and the common electrolyte used in DSSCs. The reason relies on the shorter charge transfer path at the dye/Cu$_2$S interface, and the avoidance of degradation/incompatibilities between the electrode and electrolyte [134].

In 2021, Li et al. also reported a charging voltage decrease of 0.12 V in a photo-assisted Li$-$S battery [135]. In this case, N719 dye was covered by a 16 $\mu$m of a S layer (see SEM image in Figure 3B) that acted as the energy storing component. Its surface area and conductive properties were enhanced by ball-milling sulfur, carbon nanotubes and binder all together. This is favored also because of the increased roughness and porosity of the sulfur layer that can be observed in the SEM images. However, the capacity faded along charge–discharge cycles due to the dissolution of polysulfide mediator product.

### 3.2 Transition metal oxide-based semiconductors

#### 3.2.1 Titanium oxide

Titanium dioxide (TiO$_2$) is a well-known n-type semiconductor due to its interesting properties: high stability, nontoxicity, biocompatibility, light absorption, and high electron mobility [136, 137]. It exists in three forms: anatase, rutile, and brookite. Rutile is the most used structure because it is chemically more stable, and scatters white light more efficiently compared to anatase. However, anatase shows enhanced surface chemistry and a higher conduction band-edge, which makes it more suitable for photocatalytic applications [138, 139]. One way to increase the surface area and the diffusion coefficient and decrease charge recombination is through synthesis of nanostructures (nanotubes [140, 141], nanotube arrays [142], nanobelts [143, 144], nanowires [145], nanowire arrays [146], mesoporous films [147, 148], etc.). TiO$_2$ nanostructures provide more active sites and facilitate reactions or interactions between the electrode and the active species. These interactions occur mainly on the surface and are therefore very dependent on nanostructure morphology [149–151]. Their properties and photocatalytic activity will vary depending on the particle size, shape, degree of crystallinity and ratio of anatase to rutile [150]. The main drawback is limited absorption in the visible range, which hinders the generation of photocurrent under solar illumination. Because of its remarkable properties, TiO$_2$ has found numerous applications, including photocatalytic degradation of pollutants [152], hydrogen generation [153], photovoltaic devices (solar cells [154], batteries [155] and capacitors [156]), air purification [157] and antimicrobial uses [158]. It has also been widely used as electrode material in rechargeable batteries [159–162] and, more recently; it was also employed in PBATs.

In 2017, Nguyen et al. designed a photocathode based on a mesoporous anatase-TiO$_2$ thin film of 280 nm in thickness [163], for an integrated Li-ion photobattery. In the SEM-FEG (Scanning Electron Microscopy-Field Emission Gun) top image (Figure 4A) a 3-dimensional (3D) interconnected network with pores of an average diameter of 17 nm with a high degree of pore organization was observed. However, the pore diameter decreases with the depth of the layer until a minimal diameter of 12 nm is achieved next to the interface with the fluorine-doped tin oxide (FTO) substrate. This morphology helps with charge separation and transport of both electrons and ions, which results in enlarged capacity in comparison with a non-mesoporous nanostructure (240 mA h g$^{-1}$) when
illuminated and in the dark (180 mA h g\(^{-1}\)). This is explained by insertion of Li\(^+\) ions into the TiO\(_2\) network, forming first a Li-poor phase (tetragonal Li\(_a\)TiO\(_2\), 0 < \(a < 0.25\)) and Li-rich phase (orthorhombic Li\(_{0.5}\)TiO\(_2\)) that coexist during charge and discharge processes. On the other hand, the photogenerated holes oxidate Ti\(^{3+}\) to Ti\(^{4+}\), boosting the lithium ions extraction at the same discharge rate \([164]\). When the battery is discharged under illumination, Li\(^+\) has been extracted and inserted simultaneously, which would allow for a theoretically-infinite capacity (see Figure 4B and C) without any signs of electrode deterioration. These results are in agreement with previous reports \([165]\). Furthermore, the authors suggest that surface plasmon resonance effect of lithiated nanocrystals might have a noticeable impact on the titanium dioxide oxidation process \([166, 167]\), which warrants further studies.

Another strategy to increase the photocurrent and consequently the capacity is the synthesis and application of ultralong TiO\(_2\) nanobelts (80–110 nm wide, 10 nm thick...
and 20 μm long) [168] in all-vanadium RFB. The authors describe the effect that stirring has on the nanostructure and morphology of TiO₂ nanobelts and their advantages versus conventional nanospheres. It was shown that raising the stirring speed caused an increase in the length-to-diameter ratio. As a result, crystallinity, light scattering and absorption are greatly enhanced while charge recombination and the specific surface area decreases [169, 170]. The porosity of the semiconductor layer had also a positive effect in the interaction with the electrolyte, amplifying the photogenerated current. In addition, treatment with TiCl₄ shifted the absorption of TiO₂ to longer wavelengths, improving photogenerated charges even more, showing 22% incident photon-to-current efficiency (IPCE) without any external bias. Additionally, the TiCl₄ treatment also improved electron diffusion and charge separation, reduced charge recombination and generated more exposed high-energy facets acting as reactive sites for the oxidation of active redox vanadium-based species in the electrolyte (see Type II belt, Figure 4D). This is highly beneficial for RFBs where the working mechanism fully relies on redox reactions between the electrodes and the liquid electrolytes.

In contrast with the previous example, Gong et al. reported TiO₂ nanorod arrays as the photoactive material in the PE for Li–O₂ batteries that are shorter and thicker (200 nm in diameter and ~1 μm long). In this case, the challenge consists in boosting the performance of the OER so the formation of Li₂O₂ is reversible during the charging process under illumination. Rutile TiO₂ structures with the nanorod morphology grant high oxygen diffusion and complete infiltration of the electrolyte. They also provide ample space to deposit Li₂O₂ as “storing product”. The charging and discharging voltage are 2.86 and 2.65 V respectively for the first cycle, increasing to 3.03 V (charging voltage) after 30 cycles when illuminating, which is close to the theoretical voltage (2.73 V) calculated from the conduction band of TiO₂ and oxidation potential of Li/Li⁺. However, the discharge voltage increases to 2.85 V after 30 cycles. This unexpected result could be explained by an improvement on the oxygen reduction reaction (ORR) performance related with the generation of more oxygen defects which produce intrinsic changes in the rutile TiO₂ structure (i.e. formation of TiO⁻). These defects are a consequence of the photogenerated electrons during the charging step that would reduce TiO₂. It is well known that defective metallic oxides provide much higher ORR and OER performance than their high crystalline counterparts [171–173]. In 2020, Han et al. proposed a photo-rechargeable seawater battery with two compartments utilizing sodium metal electrode as anode and TiO₂ nanotube arrays as photo-cathode [174]. Pure anatase phase annealed at 500 °C exhibited the largest photocurrent compared to mixed anatase-rutile and pure rutile because of its higher crystallinity. In Figure 4E and F, the hierarchically nano-ring structure on the top and the vertically aligned nanotubes on the bottom of the TiO₂ layer can be observed from the SEM top-view and cross-section images. The nanotubes have an average diameter of 100 nm, a wall thickness of ~20 nm and a length of ~800 nm. The 1D nanostructure promotes high electron mobility and the high surface area at the outer part enhances light absorption and contact with the electrolyte. The authors observed that the morphology, crystallinity, and crystal phase of TiO₂ nanotubes are dependent on the annealing temperature. Formation of clusters and morphological disorders and decrease in porosity were noticed when annealed at temperatures higher than 750 °C [175]. It is important to note that, the morphology, crystallinity and crystal phase of nanomaterials are generally dependent on the annealing temperature. In the two-electrode system based on this PE, the charge and discharge voltages were 2.65 and 2.50 V, respectively.

Although TiO₂ has proved to be a promising candidate for photobatteries, its poor response in the visible-light spectra originating from its large bandgap and the high charge recombination rate hinder its performance in photoelectrochemical devices. Designing heterostructure composites by combining TiO₂ with other semiconductors, dyes or plasmonic materials can effectively overcome the abovementioned limitations and boost the redox reaction kinetics. Many examples have been reported over the last years in fields such as photocatalytic degradation of anti-biotics [176], solar cells [177], and solar fuel generation [178]. Some publications demonstrated the successful design of TiO₂-based heterojunctions as the photoactive material in photo-rechargeable batteries. For instance, TiN/TiO₂ composite nanowires [179] and TiO₂–Fe₂O₃ heterojunction [180] positively reduced the overpotential to 0.19 V with a round-trip efficiency of 94% for the first composite and 86% after 100 cycles for the later. Tong et al. proposed TiO₂ nanotube arrays with gold nanoparticles in a photo-assisted Li–O₂ battery with 100% Coulombic efficiency mostly due to photocatalytic processes that effectively reduced the overpotential [181]. Among all the TiO₂-based nanomaterials, TiO₂ nanorods and nanowires so far exhibited the highest round-trip energy efficiencies due to the higher surface area compared to other nanostructures (NPs or mesoporous network), exposing a greater number of active sites, and enhancing light harvesting.
3.2.2 Hematite (Fe₂O₃)

α-Fe₂O₃ is one of the most Earth-abundant metal oxides and is thermodynamically more stable than other iron oxides in the presence of oxygen. It is chemically stable over a wide pH range, of low-cost and sustainable, and has a relatively narrow band gap of 2.1–2.3 eV, which is beneficial for light absorption in the visible range of the spectrum. It is considered an n-type semiconductor with magnetic properties [182, 183]. It has been used in many fields, such as photocatalysis, water-splitting, CO₂ removal, energy storage systems, and gas sensing [184–186].

The known nanostructures of α-Fe₂O₃ are nanorods [186], nanorods arrays [187, 188], nanoflowers [189], microwires [190], nanowires [191], nanotubes [185, 188], nanostructures [192], and nanoparticles [193] among others.

Liu et al. and Gong et al. presented α-Fe₂O₃ nanorods as PE in Zn–air and Li–O₂ batteries respectively [85, 86]. They performed a hydrothermal synthesis followed by two-and one-step annealing processes, respectively. The annealing at 800 °C ensures the doping of Sn into the Fe₂O₃ nanostructure to increase its conductivity. However, nanorods that went through two annealing processes (550 °C for 2 h and 800 °C for 10 min) have smaller diameters and look highly ordered, suggesting that this intermediate step is beneficial to control the size and shape of α-Fe₂O₃ nanorods. They show an average diameter of 70 and 80 nm, and film thickness of ~350 and 450 nm, respectively (Figure 5A and B). Plenty of space was observed between nanorods, which is considered essential for electrochemical reactions on the PE surface. This is specifically relevant for the photogenerated holes, which have a strong ability to oxidize water into oxygen. This structural feature thus facilitates OERs which have sluggish kinetics in conventional rechargeable batteries. The photogenerated electrons in the CB of the semiconductor are transferred to the metal electrode for reduction of the metal ion (M⁺ + e⁻ → M(0)). The highly stable surface morphology does not change with charge and discharge cycles in both cases, which was confirmed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). As a result, it delivers a stable current density over time.

α-Fe₂O₃ PE shows absorption in the visible range with an absorption edge of ~600 nm and an optical bandgap of ~2.10 eV. Both works show an improvement in the charging voltage, thus, in the round-trip energy efficiency up to 70.3 and 87.7%, respectively. α-Fe₂O₃ nanorods PE in the Zn–air photobattery yielded charge and discharge voltages of 1.64 and 1.15 V for several cycles over 50 h under illumination [86]. Gao et al. reported a reduction of the charging voltage, decreasing from 3.96 to 3.15 V under illumination, with a discharge voltage of 2.56 V, resulting in an energy efficiency increase of 16.6% for the Li–O₂ system [85].

Due to a reduction in resistance of the charge transfer along the electrode and its interface with the electrolyte, α-Fe₂O₃ nanorods show enhanced photoelectrochemical response when they are highly ordered [194]. The same configurations were tested using BiVO₄ nanoplates with no positive results due to their dissolution in alkaline environments and aggressive photocorrosion.

In 2016, Wedge et al. utilized hematite synthesized by spray pyrolysis as the photoanode for aqueous alkaline SFB. They used ferrocyanide and anthraquinone-2,7-disulphonate (AQDS) in a solution of NaOH as electrolytes in the anode and cathode side respectively divided by a conductive cation membrane [195]. Since hematite suffers from back electron recombination [196, 197], the photogenerated electrons reduce ferricyanide instead of AQDS. Therefore, the experimental charging voltage under illumination is lower than expected taking into consideration its energy levels (CB and VB) under alkaline conditions. Polyaniline (conjugated polymer formed by blocks of benzyl rings linked by an amine) was deposited on the surface of hematite to overcome this issue and compare the results with bare and annealing-only samples. It was proven that low-temperature steam annealing significantly reduces surface defects [198], creating a smoother hematite layer that facilitates the deposition of a more homogeneous layer of polyaniline. FE-SEM (see Figure 5C) was performed to evaluate the morphology of the samples showing granular particles of different sizes ranging from 0.1 to 0.5 μm for annealed and coated samples and more irregular particles for bare hematite. The polyaniline layer must be thin to allow light absorption by the hematite. This coating enhances the photoelectrical response because its lowest unoccupied molecular orbital (LUMO) level is lower than the CB of the α-Fe₂O₃. This prevents the previously mentioned back electron recombination to the ferrocyanide electrolyte while allowing the holes from the VB to move to its HOMO level. Although the solar-to-chemical-energy conversion efficiency for this SFB is still rather low (0.08% for the coated hematite), this work shows the possibility of a pure solar rechargeable redox flow battery. The same year, Nikiforidis et al. published a Li–I₂ SFB with granular nanoparticles of hematite photocathode with a film thickness of 90 nm. In this case, the PE was synthetized by anodic electrodeposition followed by annealing at 550 °C [199]. The charging voltage under illumination was reduced by 0.66 V, with an increase in the energy efficiency of ~21% when compared with the same device under dark conditions. However, unlike the previous example, no full charge was observed in the
absence of an external bias; charging fully under illumination could only reach up to 10% state-of-charge (SOC). The SEM image in Figure 5E depicts the PE surface after electrodeposition of the hematite and annealing, which shows many particles with an average diameter of 33 nm. The surface appears to be less smooth with less defined nanoparticle shape compared to the PE described by Wedege et al. The reduced surface area of the granular nanoparticles compared to nanotubes or nanowires [200] in contact with the electrolyte decreased photocatalytic activity which resulted in lower energy efficiency and the impossibility of unbiased charge. The low temperature steam annealing and the deposition of polyaniline had a positive effect on the PBAT performance.

PEs that employed α-Fe₂O₃ nanorods obtained higher specific capacity values and more stable devices in comparison to α-Fe₂O₃ NPs, but lower overall device efficiencies. However, it should be noted that the described systems are quite different (Zn–O₂, Li–O₂, Li–I₂, and RFB) and they do not show standardized experimental parameters to allow accurately comparing the performance of these PBATs and indisputably assessing the effect of morphology.

3.2.3 Tungsten trioxide

The transition metal oxide tungsten trioxide (WO₃) is an n-type semiconductor with a bandgap of ~2.6–3.0 eV [201].

Figure 5: Structure and performance of hematite-based photoelectrodes. (A) SEM image of α-Fe₂O₃ film (scale bar 1 μm) [172]. Copyright 2019, Springer Nature. (B) SEM image of α-Fe₂O₃ film [173]. Copyright 2020, Elsevier. (C) Field emission scanning electron microscope (FE-SEM) images of bare, annealed and coated α-Fe₂O₃. (D) Capacity data for 10 cycles of charge–discharge cycles with a constant current density of 20 mA cm⁻² [175]. Copyright 2016, John Wiley and Sons. (E) Top-view SEM and digital (inset) images of hematite granular NPs [176]. Copyright 2016, American Chemical Society.
It responds to visible light, making it an optimal PE candidate. WO$_3$ nanoparticles have high specific surface area, impressive hole diffusion length, and high electron mobility (due to good surface permeability), and are nontoxic, as well as being chemically and photochemically stable [202]. WO$_3$ is often present as sub-stoichiometric oxide (WO$_{3-x}$) due to the presence of numerous oxygen vacancies, which affects the electron density and its conductivity [203–205]. Monoclinic is the most stable phase of WO$_3$ at room temperature and has the greatest absorption in the visible range of the spectrum among all of its phases, making it more desirable for photocatalytic applications [206, 207]. Among the most common WO$_3$ nanostructures, we can find nanorods, nanosheets, 3D nanostructured *papilio paris* and thin films being used by themselves or as part of heterojunctions with other materials [208–212]. They have been widely used as photodetectors [213, 214], as photocatalysts [215, 216], for water splitting [212, 217] and in gas sensors [218, 219]. On top of these uses, there have been several publications where WO$_3$ was used as a PE in PBATs.

In 2019, Feng et al. reported WO$_3$ nanowire (NWs) arrays grown *in situ* on carbon textiles in Li–O$_2$ batteries [220]. By controlling the reaction time of the hydrothermal synthesis, they achieved an optimal coverage of the tungsten oxide precursor on the surface of carbon fibers at 16 h. A heating treatment was subsequently needed to control the crystalline phase of WO$_3$ [201]. Generally, the greater the degree of crystallization, the less active sites and surface area WO$_3$ has negatively affects photochemical reactions [221]. Three samples were prepared at different temperatures under air and/or nitrogen (see Table 1). The samples prepared under nitrogen atmosphere have more defects, which is detrimental for hole diffusion and electron mobility. However, all of them displayed absorption in the range of 500–800 nm due to oxygen vacancies [222]. WO$_3$-AN is the best PE candidate since it has a smaller bandgap (2.63 eV), which leads to more visible light absorption, charge separation and fewer defects as confirmed by XPS measurements. Monoclinic WO$_3$-AN absorbs more visible light than the hexagonal structure and also has fewer defects, which grants more beneficial hole diffusion length and electron mobility. Consequently, we can expect a higher rate. SEM image (Figure 6–C) shows WO$_3$ NWs grown vertically, covering the surface of the carbon fiber uniformly, and having a high surface area (high number of active sites, very beneficial for the photocatalytic ORR). It shows the lowest charging potential (~3.55 eV) under illumination, maintained over 100 cycles, demonstrating high stability under light irradiation. This was attributed to its monoclinic phase and relatively fewer defects.

In 2020, the same group reported a photocathode made up of WO$_3$ NW arrays decorated with g-C$_3$N$_4$ for Li–O$_2$ batteries [223]. The morphology of WO$_3$ NWs arrays is highly comparable to their previous report. The advantage of this heterojunction is facilitating the separation of the electron–hole pair and inducing faster migration of charges. Thus, charge recombination is avoided. It also increases visible absorption, which enhances catalytic performance. Furthermore, g-C$_3$N$_4$ acts as a co-catalyst, providing new active sites for the ORR and lowering the overpotential 3.69 V (vs 3.99 V from WO$_3$ NW array).

### 3.2.4 Vanadium oxides

Vanadium is considered a highly abundant element in the Earth’s crust [224]. It shows multiple oxidation states and presents an elevated number of crystalline structures with different oxygen coordination [225, 226]. The most common crystalline structures are VO$_2$, V$_2$O$_5$, and V$_5$O$_7$. The two first ones have already been used as cathode materials in Li–ion batteries [227–229], showing high specific capacity and energy density as well as good photocatalytic properties, which also make them promising materials for use in photobatteries. De Volder’s group has published several articles during recent years using vanadium oxides as PEs in PBATs.

In 2020, his group reported a photo-to-electric conversion efficiency of 1.2% with a system containing V$_2$O$_5$ nanofibers mixed with poly(3-hexylthiophene-2,5-diyil) (P3HT) and reduced graphene oxide (rGO) as PE, in Zn-ion battery [59]. The photogenerated electrons travel to the Zn electrode while holes are blocked by P3HT and accumulate in the photocathode (Figure 7A). They observed a clear increase in capacity when the PE is exposed to light. Furthermore, the capacity of the battery increases under illumination even during the discharge process. V$_2$O$_5$ nanofibers show orthorhombic structure with diameters of 50–100 nm with an interplanar spacing of ~0.204 nm (see SEM and TEM images in Figure 7B). The optical bandgap of 2.2 eV ensures light absorption in the visible range. The advantages of using V$_2$O$_5$ nanofibers versus other nanostructures include higher conductivity along the nanofiber.

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**Table 1: WO$_3$ synthesis conditions and structure [200].**

<table>
<thead>
<tr>
<th>Name</th>
<th>Heating temperature (°C)</th>
<th>Time (hours)</th>
<th>Conditions</th>
<th>Phase</th>
</tr>
</thead>
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<tr>
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<td>2</td>
<td>Air</td>
<td>Hexagonal</td>
</tr>
<tr>
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<td>550</td>
<td>2</td>
<td>Nitrogen</td>
<td>Monoclinic</td>
</tr>
<tr>
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<td>2</td>
<td>Air</td>
<td>Monoclinic</td>
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<td></td>
<td>(2) 550</td>
<td>2</td>
<td>Nitrogen</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>
length and larger surface area, which will provide more active positions for interactions with other molecules or ions [114]. Combination with rGO provides an optimal lithium-ion diffusion and electron transfer to the cathode and high cycling stability. It also impedes the agglomeration of nanostructures [230].

In 2021, Boruah et al. of the same group reported the same photocathode structure in Li-ion batteries (rGO, P3HT, and V2O5 nanofibers) [66]. The difference was in the nanofibers’ diameter, which was found to be between 20 and 50 nm (see Figure 7C), considerably smaller compared to their previous work, and an increase in the interplanar spacing up to 0.34 nm. During charge, the oxidation state of vanadium changes due to the accumulation of the photogenerated holes, releasing the Li+ that was intercalated in the V2O5 nanofibers, Li+ travels to the anode, where the electrons are been collected, and it is reduced to Li metal. V2O5 nanofibers experience reversible phase transformations when they are oxidized [231, 232], something that takes place during the charging and discharging steps. These phase transformations can be observed because of changes in the band gap energy. This is visible by looking at the color change of the photocathode in the charge and discharge states and it is due to lithium insertion/removal [233], as it is shown in Figure 7D. The achieved photo-to-electric conversion efficiency with this system was 2.6% under 455 nm illumination and 0.22% for 1 sun illumination without the need for an external energy source. The photocharging voltage was 2.82 V, achieving a nearly constant 2.45 V when discharging under illumination. It may be noted that a direct comparison between two different metal-ion batteries should be avoided because of the potential difference of the metal electrodes. However, we can say that nanorod and nanofiber vanadium oxide-based PEs confer higher photo-to-electric conversion efficiencies and allow the device to operate without the need of applying an external bias.

De Volder’s research group published two more articles using vanadium oxides with Zn-ion batteries. The first one replicates the previous report except for removing P3HT trying to reduce the overall cost of the device [234]. In this case, rGO was mixed with VO2 instead of V2O5. They achieved double capacity, higher rate capability, and better capacity retention over 1000 cycles (of about 90%). VO2 nanorods have a monoclinic structure and an interplanar spacing of ~0.35 nm [235, 236]. The band gap of VO2 nanorods was obtained from UV–vis absorption measurements, showing an indirect and direct band gap of 2.3 and 2.53 eV. They were higher than that of V2O5 nanofibers, and thus exhibited a blue-shift in the absorption spectra. They observed greater intercalation of Zn2+ in V2O5 nanofibers during the discharge process due to the photogenerated charges that improve the capacitive contribution of the photocathode, leading to an increase in
the Zn\(^{2+}\) diffusion kinetics. This is due to the structure of the framework with relatively large tunnels of 0.82 nm approximately along the \(b\)-axis and 0.5 nm along \(c\)-axis [237] (Figure 7E). In this case, the insertion of Zn ions does not change the optical band gap. However, the photo-to-electric conversion efficiency achieved was only 0.18%. Afterward, they published another paper on the Zn-ion battery [234] where they showed an increase in the photoconversion efficiency up to 0.51% (at 455 nm illumination). In this example, VO\(_2\) was deposited on top of ZnO, which acted as hole collector instead of rGO. The improvement in efficiency was due to a more efficient charge separation with ZnO, mainly because of the direct deposition instead of physical mixtures used in the previous publications. The battery capacity in this last work is two times higher than those using V\(_2\)O\(_5\), but its efficiency was lower.

The combination of vanadium oxides and carbonaceous materials, such as graphene, carbon nanotubes (CNTs), and carbon fibers, was extensively studied. A thin layer of carbon coating on vanadium oxides was found to have improved cycling stability and electrochemical properties for LIBs [181]. However, the thickness of carbon coatings needs to be carefully controlled, since thicker coatings might impede the diffusion of Li ions [182]. In this regard, mesoporous carbon layers are highly desired to enhance the ion transfer between vanadium oxides and electrolytes [183]. The stacked structures of vanadium oxide and rGO were found to exhibit

**Figure 7:** Structure and performance of vanadium oxides-based photoelectrodes. (A) Photocharging mechanism of Zn–air PBAT. (B) SEM images of V\(_2\)O\(_5\) nanofibers and inset HR-TEM image of Zn–air PBAT [69]. Copyright 2020, Royal Society of Chemistry. (C) SEM image of V\(_2\)O\(_5\) nanoﬁbers and inset HR-TEM image of Zn–air PBAT [69]. Copyright 2020, Royal Society of Chemistry. (C) SEM image of V\(_2\)O\(_5\) nanoﬁbers and inset HR-TEM image of Zn–air PBAT [69]. Copyright 2020, Royal Society of Chemistry. (D) Initial discharge–charge curve using an optical-cell, images showing the change in color as a function of the SOC, and ex situ absorbance spectra of the PE at different SOC of V\(_2\)O\(_5\) nanofibers in Li-ion PBAT [211]. Copyright 2021, American Society of Chemistry. (E) SEM image of VO\(_2\) nanorods [215]. Copyright 2021, Royal Society of Chemistry. (F) Photocharging and discharging mechanisms of Na-ion PBAT [216]. Copyright 2017, John Wiley and Sons.
enhanced capacity and cycling stability [184]. Also, the fabrication of nanocomposites promotes electrolyte diffusion and ion transfer, improving electrochemical kinetics [238]. Structural stability can also be enhanced by compounding multiple strategies such as surface coating and particle-supporting.

### 3.2.5 Molybdenum oxide

Like vanadium oxides, molybdenum oxides also have light absorption in the visible range of the spectra, several crystal structures, and can incorporate alkali ions in their structures [239, 240]. MoO₃ has attracted great attention in the last decades due to its nontoxic nature and remarkable performance in fields such as photovoltaics [261], energy storage [242], gas sensing [243], and catalysis [244]. It is an n-type semiconductor whose oxygen composition varies as follows: MoO₃, where 2 < x < 3. These variations can induce changes in the physicochemical properties (i.e. light absorption, electrical conductivity, and localized surface plasmon resonance) [240, 245–247]. Lou et al. reported a MoO₃-based photoanode in Na-ion battery that can be charged without applying an external bias [248]. MoO₃ nanostructure is formed by particles with platelet morphology and an average particle size of 306 ± 170 nm [249]. Na⁺ ions from the electrolyte neutralize the photogenerated electrons and are stored in the lattice structure of the MoO₃ while the holes move to the electrode surface to oxidize water to oxygen. The process takes place in two steps as the voltage increases. During charge, cation intercalation distorts the orthorhombic α-MoO₃ phase first to a sodium bronze phase (Na₀.33MoO₃), followed by the formation of NaₓMoO₃ (0.33 < x < 1.1) (see Figure 7F). The intercalation/deintercalation is only partially reversible, confirmed by XRD and XPS analysis where the phase composition of the photoanode was shown to be Na₀.35MoO₃ after discharge, resulting in a change in the Mo oxidation state equivalent to Na⁺ insertion [250, 251]. Based on these facts, it was demonstrated that the two mentioned phases coexist after 2 h of discharge. Although the authors report no sign of physical deterioration at fast Na⁺ intercalation rates, MoO₃ dissolves with time, hindering the stability of the photobattery. More research must be performed in order to address this issue.

### 3.2.6 Cobalt oxide

Cobalt oxides are inexpensive and same as many metal transition oxides; they can delocalize electrons that previously occupied O 2p orbitals to ease the oxidation of Co³⁺ into Co⁴⁺ during OER [252, 253]. Their catalytic activity can also be tuned by introducing oxygen vacancies, among other strategies [252]. Because of these beneficial properties, the use of cobalt oxides has been explored in photocatalysis as well as EESs, including secondary Li-ion batteries [254, 255]. Spinel Co₃O₄ is a p-type semiconductor with a direct and indirect bandgap of 1.4–1.8 and ∼2.2 eV, respectively. Cobalt is present in two oxidation states, where Co⁴⁺ has an octahedral structure and Co³⁺ is tetrahedrally coordinated with oxygen ions, forming close-packed face centered cubic lattice [256]. When Co₃O₄ is exposed to light, it becomes a highly active, releasing super-oxidizing species that reacts with OH⁻ and H₂O. In 2019, microrod structures of spinel-like Co₃O₄ interconnected with other Co₃O₄, spherical particles of a size of 25 nm were introduced as a bifunctional electrode in Zn–air PBATs [257]. Its mesoporous structure assists the ORR and OER photocatalytic reactions which involve OH⁻ groups during charge/discharge under illumination. Despite its high stability, the difference between charge and discharge voltage, as well as the difference in specific capacity under dark and light conditions are not significant.

### 3.3 Chalcogenide-based nanomaterials

Metal chalcogenides are well-known materials usually referred to MXₙ, where X represents an element from VI A group (X: S, Se and Te) and M a transition metal. MXₙ are 2D materials with large interlayer distances [258, 259]. They consist of a hexagonal dense layer of M atoms sandwiched between two layers of X atoms. Because of large interlayer spacing and weak van der Waals interaction between layers, metal ions can intercalate into their structure [260, 261]. Because of this, they have already been used as electrodes in Li- and Na-ion batteries [259, 261]. However, they experience lower volume expansion which can be detrimental. They can undergo multi-electron redox reactions and have a fast ion diffusion rate due to the lability of the M–X bond. The bandgap can vary from 0 to 2 eV depending on elemental composition, the number of layers and the presence of doping agents, which allows for tailoring properties according to the desired application [258].

Cadmium sulfide (CdS) is the most used chalcogenide. It is an n-type II–VI semiconductor that has been widely employed as a photocatalyst because of its light absorption capabilities in the visible range. It has high conductivity in addition to its low-cost synthesis. It can be used with other metals or coupled with other semiconductors to prevent electron–hole recombination [262–264]. Its VB and CV positions are suitable to use with vanadium redox species in SFBs. Two examples are reporting its use as a photoelectrode in this type of PBAT. Peimanifoard et al.
reported two and three-electrode SFBs using $V^{3+}/V^{2+}$ and $VO^{2+}/VO^{2+}$ as electrolytes [265]. The photoelectrode is formed by CdS clusters covering the surface of multiwalled carbon nanotubes (MWCNTs), as Figure 8A displays. The clusters are attached to MWCNTs, providing a higher surface area that will facilitate contact with the electrolyte, boosting the photocatalytic reaction. Under illumination, the photogenerated electrons are successfully transferred to the counter electrode and reduced $V^{3+}$ to $V^{2+}$; while the holes oxidize $VO^{2+}$ into $VO^{2+}$ in the electrolyte. Nevertheless, it is necessary to apply an external bias. The photo-to-electric conversion efficiency achieves 2.12% when the voltage is 1.38 V (vs the CE) (vs Ag|AgCl| KCl) for the two-electrode system. The photoelectrode does not present photocorrosion after 1 h of on-off cycles, a common problem when using CdS. It is brought on by photogenerated holes that fail to be removed in time, causing degradation and dissolution [266–268]. A similar system was developed by Azevedo et al., which consisted of a two-electrode SFB using $V^{3+}/V^{2+}$ and $V^{3+}/VO^{2+}$ as active species in the electrolyte and carbon felt as a cathode [269]. The photoactive material was based on CdS nanostructures with 50 nm cauliflower shape (Figure 8B) that were electrodeposited as a thin and compact layer of 200 nm. The changes in the deposition potential gave them different morphologies. These cauliflower-like nanostructures yielded the highest photocurrent performance, owing to their rougher morphology and increase number of active sites for photocatalytic reactions. In order to improve the performance of the battery, a layer of compatible semiconductors was deposited over CdS, TiO$_2$ and CdSe were chosen since they have photocatalytic activity in the studied system and have been proven to be stable in the voltage range where the battery functions.

Figure 8: Structure and performance of chalcogenide-based photoelectrodes. (A) SEM image of MWCNT/CdS PE [246]. Copyright 2015, Elsevier. (B) SEM image of CdS photoanode [250]. Copyright 2016, Elsevier. (C) Charging mechanism of Cd/Pt Li–S PBAT. (D) Discharge curves at different irradiation times. (E) Specific discharge capacity versus irradiation time [95]. Copyright 2015, John Wiley and Sons. (F) Cross-section and (G) top-view SEM SE images of CdS-coated WO$_3$ film, inset corresponds to high-magnification SEM SE image. (H) Discharge capacity versus cycle number [88]. Copyright 2019, John Wiley and Sons. (I) TEM image of CdSe/ZnS QDs@CNT composite [259]. Copyright 2018, Elsevier. (J) Electrochemical performance of solid-state Li-ion O$_2$ battery with (blue line) and without (black line) illumination at 0.026 mA cm$^{-2}$. (K) Photo-assisted charge curves of photo-assisted solid-state Li-ion O$_2$ battery based on the voltage at the half-charge capacity point. (L) SEM image of ZnS@CNT composite [260]. Copyright 2018, Elsevier. (M) SEM and (N) TEM images of SnS$_2$ [261]. Copyright 2019, Royal Society of Chemistry.
Despite TiO$_2$ having been widely explored as a protective layer for other semiconductors, including CdS, it did not generate any benefits in this system. The CdS/CdSe PE generated three times more photocurrent ($1.4$ mA cm$^{-2}$ at $0$ V vs $0.47$ mA cm$^{-2}$) compared to bare CdS. However, none of them was able to provide the sufficient potential to fully charge the SFB without an external bias or enough stability to measure charge/discharge cycles for more than $5$ min. More efforts need to be put in this regard by including a sacrificial agent or increasing the pH of the electrolyte [274, 275]. Because of the differences in the counter electrodes and electrolytes, it is not possible to make a straightforward comparison between the above-mentioned SFBs. However, the cauliflower-like CdS nanostructures allowed photocharging of the battery until $90\%$ SOC was achieved. We can conclude then, that this specific morphology allows for better battery performance by increasing the surface area, shortening the diffusion paths, and exposing more active sites, which improves the reaction kinetics with the redox-active species and reduces charge recombination [276, 277].

To improve the stability and performance of CdS, Li et al. proposed the introduction of Pt as a co-catalyst for lithium–sulfur PBATs [119]. The PE is composed of CdS decorated with Pt NPs of $4–8$ nm in size. The $S^{2-}$ ions produced during the discharging process are oxidized into polysulfides ($S_{2n}^{2-}, 2 \leq n \leq 8$) by photogenerated CdS holes during the charging process and the electrons are transferred to the Pt nanoparticles. These electrons will reduce $H^+$ from the electrolyte to produce $H_2$, a valuable fuel (Figure 8C). Hence, this singular system can store energy electrochemically and generate $H_2$ at the same time. Pt NPs can lower the overpotential for water splitting and sulfide-based electrolytes are well known as efficient sacrificial agents that can be oxidized by the photogenerated holes in CdS. This helps avoid recombination between holes and electrons in the semiconductor and prevents corrosion by simplifying the system [263, 278, 279]. In the end, $792$ mA h g$^{-1}$ of discharge capacity are obtained at $0.1$ mA cm$^{-2}$ rate after $2$ h under illumination, being proportional with the irradiation time. The hydrogen evolution rate is $3.04$ mmol g$^{-1}$ h$^{-1}$. However, insoluble elemental sulfur ($S_8$) is detected after $4$ h of irradiation, compromising the battery stability and the cycling performance (Figure 8D and E).

Demopoulos’s and Zaghbi’s groups designed a photo-absorbing and energy storing bifunctional photoelectrode based on WO$_3$ coated with TiO$_2$ and sensitized by CdS for two different types of two-electrode systems: Li and Na-ion intercalation batteries [113, 280]. As explained earlier, WO$_3$ allows the intercalation of Li or Na ions in its structure, enabling charge storage under illumination. This is also a well-studied process in Li-ion batteries [220, 223]. Since optical absorption of WO$_3$ is limited by its bandgap, a light sensitizer can help improve the photocharging process. WO$_3$ (coexisting cubic and hexagonal phases) was formed in situ on top of a layer of FTO and treated with TiCl$_4$ that leads to the formation of a thin layer of TiO$_2$ after heating treatment. TiO$_2$ was chosen due to the favorable alignment of its CB with that of WO$_3$, facilitating charge transfer and reducing the recombination of holes and electrons [102]. CdS acts as a sensitizer; with a bandgap of $2.5$ V versus Li/Li$^+$ ($-4$ eV vs vacuum), it has visible light absorption and can efficiently transfer the electrons to WO$_3$ during the charging step under illumination. Li or Na ions will compensate for the negative charge due to the accumulated electrons from CdS by intercalation into its crystal structure. The photogenerated holes are collected by sacrificial hole scavengers or polysulfide species ($I_3^-/I^-$ from Li in the Li-intercalation battery and, Na$_2$SO$_3$ and Na$_2$S in the Na-ion system). For the Li-intercalation photobattery, SEM images (Figure 8F and G) display the complete infiltration of CdS in the porous structure of WO$_3$, forming a low-crystalline structure with a smooth surface; also confirmed by energy-dispersive x-ray spectroscopy (EDS), XPS, and XRD analysis. This morphology seems to be favorable for light absorption and charge transfer to WO$_3$, but it hinders the Li ion diffusion. After several photocharging-discharging cycles, the smooth CdS coating cannot be observed. This is the result of degradation by the electrolyte and photocorrosion, which eventually lead to a decay in the photocharging efficiency. However, this degradation is beneficial since it exposes WO$_3$ to more Li ions and increases interfacial intercalation. As a result, the stability of the system is compromised but self-discharging over time can be observed (see Figure 8H) [113]. In the Na-ion photobattery, the CdS layer remains stable after several cycles because of the introduction of Na$_2$SO$_3$ and Na$_2$S as hole scavengers. This system achieved $0.3\%$ of overall photo-to-electric energy conversion-storge efficiency [280]. Nevertheless, the scavengers need to be continuously replenished, and the Pt counter electrode is not stable in sulfide electrolytes [281, 282]. For this reason, they replaced Pt with Cu$_2$S electrode and added $S^{2-}/S_n^{2-}$ as a nonsacrificial redox couple. The resulting device gained stability and the photocurrent was greatly enhanced because of the higher catalytic activity of the new electrolyte [280]. More efforts must be put towards avoiding CdS’s photocorrosion and degradation by the electrolyte, which compromises the battery stability.

In order to decrease the overpotential caused by Li$_2$O$_2$ in Li–O$_2$ photobatteries, Veeramani et al. developed a nano-composite photocathode containing CdSe/ZnS QD@CNT. Both CdSe and CdSe/ZnS present the same cubic zinc blende structure [283]. The average particle size was
When tested in a two-electrode configuration of 99.8% over 100 charging/discharging steps. The PE was investigated in a Li/GeSe half-cell, where the surface of the PE. The electrochemical characterization of the PE can be attributed to the surface passivation effect of ZnS, making them more robust (useful in aggressive environments with oxidation and reduction reactions), hindering recombination of photogenerated electrons and holes as well as increasing photoluminescence [286–288].

The ZnS@CNT composite was proposed by Liu et al. for solid-state Li-ion O2 photobatteries [289] to address the overpotential issue present in these systems. Even though the CB of ZnS and CdSe@ZnS QDs give them the same theoretical charging voltage under illumination, the actual charging voltage of the ZnS system was 2.08 V (2.65 V for that of CdSe@ZnS QDs), presenting an electric energy efficiency of ∼113%. The charge voltage remains stable at 2.2 V after 50 cycles (see Figure 8) and K. The diffraction peaks of ZnS revealed the hexagonal structure and SEM images (Figure 8L) showed CNTs uniformly covered with spherical grain-like nanoparticles of ∼70 nm of diameter. They offer a large surface area that boosts the photocatalytic oxidation of Li2O2. In 2020, Ren et al. tested GeSe NPs as photoactive material in Li-ion photobatteries [290]. GeSe is a chalcogenide with visible light-absorbing properties, large absorption coefficient (>104 cm−1), and high electrical conductivity [291, 292]. GeSe nanostructures have already been studied in non-photo Li-ion batteries. They exhibit a high diffusion rate of lithium ions without impacting the GeSe nanostructure, particularly when they form nanoparticles with a high surface/volume ratio [293–295]. The synthesized GeSe nanoparticles had a wide size distribution (100–300 nm) with an orthorhombic crystal structure composed of folded layers that interact by van der Waals forces, where atoms within the layer are covalently bound to three neighbors [296]. The NPs were uniformly distributed on the surface of the PE. The electrochemical characterization of the PE was investigated in a Li/GeSe half-cell, where the first discharge step revealed the formation of SEI, Ge, and Li–Ge alloys [292, 293, 297] that decrease the capacity during the charging process. However, no capacity loss is observed after the second cycle, with a Coulombic efficiency of 99.8% over 100 charging/discharging steps. When tested in a two-electrode configuration with LiClO4 as the electrolyte, the battery suffers from self-discharging. Tian et al. proposed SnS2 arrays on Ti mesh as photocathode in a two-electrode redox flow system [298], SEM and TEM images (see Figure 8M and N) confirm its nanoflower- and nanowall-hierarchical morphology, with a well-layered structure because of the presence of weak van der Waals interactions between sheets (with an interlayer distance of 0.59 nm). These unique vertically oriented SnS2 arrays provide a large surface area that facilitates the contact with the liquid electrolyte and enhances light harvesting efficiency and charge transport. As a result, the PE shows good cycling capability without any apparent decay in voltage or current.

Another example of chalcogenide-based photoactive nanomaterial is molybdenum disulfide (MoS2), reported by the group of de Volder in 2021 [299]. They used the same recurring strategy by introducing an electron blocking layer between the photoactive material and a charge collector (carbon felt) to reduce the recombination of the photogenerated holes and electrons [59, 234]. The better light-harvesting properties, higher cycling stability and less toxicity of MoS2 compared to vanadium oxides make it a more suitable alternative as photoanode in Zn–air photobatteries. The reason why MoS2 is more stable after charging and discharging cycles is that the intercalation of Zn ions does not affect the semiconducting 2H phase (hexagonal structure, where Mo atoms are coordinated by six surrounding S from the upper and lower layer) of MoS2 dense nanosheets. This is the key to the photocharging process (versus 1T phase, metallic) [300–302]. Only after 500 cycles, it starts to present some cracks and its surface becomes rougher due to the formation of Zn dendrite. This resulted in a photoconversion efficiency of 1.8 and 0.2% for 455 nm and 1 sun illumination, respectively.

A mesoporous InS3@CNT/SS (stainless-steel mesh) was proposed as a photocathode in Li–CO2 batteries by Guan et al. [303]. Of the three crystalline structures of InS3, β-InS3 (spinel-like) is the one that behaves as an n-type semiconductor [304]. Its high stability, low toxicity and resistance to photocorrosion have made it an attractive candidate in photocatalysis [305–307]. InS3 nanosheets covered uniformly CNT surface with an ultrathin layer of 2–5 nm in thickness. Its porous structure (with a pore size of 3–10 nm) in the 3D-nest like CNT nanoforest exposes many active sites for photocatalytic reactions between the electrode and the electrolyte, increases light absorption and promotes charge separation. Charge and discharge voltages are 3.14 and 3.20 V, respectively under illumination. As a result, the round-trip efficiency is 98.1%, compared to 70.7% in the dark. This demonstrates the beneficial photocatalytic properties of InS3. The mechanism of the discharge step under illumination is slightly different from Li–O2 batteries. The authors proposed the formation of In+ when the photogenerated electrons travel to the surface of
3.4 Perovskite-based nanomaterials

Perovskite lends its name to the class of compounds that have the same type of crystal structure as CaTiO₃ [312]. Organic-halide perovskites have received tremendous attention over the last decade in the field of photovoltaics due to their unique properties which include tunable bandgap, high charge carrier mobility, broad absorption spectrum, long charge diffusion lengths, and high defect tolerance [313, 314]. Metal-halide-based perovskite solar cells have achieved high power conversion efficiencies of up to 25.5% [315, 316]. More recently, some publications have shown that perovskites can be also used in Li-ion or Li-air batteries [317–320]. However, it was not until 2018 that the first perovskite-like material was used in photo-rechargeable Li-ion batteries. Ahmad et al. reported two polycrystalline metal-halide-based 2D perovskites as energy conversion and storage photoanodes: cyclohexylethyamine lead iodide \((\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbI}_4\) (CHPI) and its bromine analogue, cyclohexylethyamine lead bromide \((\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2\text{PbBr}_4\) (CHPB) (Figure 9A) [321]. The organic cations sandwich the inorganic monolayers formed by \(\text{PbX}_6^{+}\) octahedral. This layered structure enhances stability compared to 3D perovskites and absorbs/diffuses Li ions effectively [322, 323]. The drop-casting deposition method was chosen so the nanostructures would grow vertically on top of the FTO substrate, allowing favorable charge transfer, increasing the porosity and promoting more efficient light interactions. Figure 9B shows the SEM image of 2D perovskite nanoplatelets that are 8–10 μm high and 320 nm thick. The energy is stored in the perovskite by ion intercalation and conversion processes [324]. Because of the 2D perovskite structure, Li⁺ ions can migrate and interact with the perovskite throughout different sites (i.e., with the ring or functional group of the organic molecule, in the bulk or the surface) [325] in a more efficient way when compared to 3D perovskites, leading to greater device performance. It was noticed that \(d\)-spacings between the interlayers measured by XRD moves from 17 to 18 Å when the discharge voltage is under 1.85 V. This proves that there is an efficient transport of Li⁺ ions between the 2D perovskite layers that contribute to the capacity [325]. In addition, it also demonstrates that the discharge processes modify the perovskite structure when the Li⁺ ions occupy empty spaces in the perovskite crystalline structure. It is observed that the intercalation occurs at 1.85 V, while the conversion reaction proceeds at 0.3 V. The latter one is responsible for the stability issues by generating SEIs and lead metal that can form an alloy with Li. This results in an irreversible change of the morphology of the layer [326] and an important decrease in the capacity/overall efficiency of the device (which was 0.034% in the best case). Because of this and the toxic nature of Pb, other metals (such as Sn or Bi) need to be leveraged for energy storing systems.

Two more recent examples of lead-free perovskite have been reported using \(\text{Cs}_3\text{AgBiBr}_6\) double perovskite [116] and \(\text{Cs}_3\text{Bi}_2\text{I}_6\) nanosheets [327] as photo-active materials. The double perovskite fulfills the basic requirements to be an adequate photoactive material, but it lacks stability since solvent crossover between compartments will eventually dissolve the perovskite. In addition, the formation of AgBr after cycling changes the morphology of the \(\text{Cs}_3\text{AgBiBr}_6\) film and it has oxygen-induced self-discharge issues, a concern in aqueous batteries with low O₂ tolerance [116, 328, 329]. \(\text{Cs}_3\text{Bi}_2\text{I}_6\) is a lead-free, all-inorganic halide perovskite that forms zero-dimensional (0-D) nanocrystals (NCS) with hexagonal packing structure where \([\text{Bi}_3\text{I}_6]^{3–}\) forms octahedral clusters surrounded by Cs⁺ ions, as can be seen in Figure 9C. The champion photovoltaic conversion efficiency of 0.43% for the first cycle includes carbon felt as the current collector and it was shown that it can be charged without any external current. Under illumination, the photogenerated current compensates for the discharge current at the studied discharge rate. Nevertheless, a drop in the discharge capacity is observed after the first cycle. If the degradation of the photobattery follows the same mechanisms as the non-photo Li-ion
reported using the same perovskite as an anode, the loss in capacity is due to SEI, the formation of Li–Bi alloys and the conversion of Bi$^{3+}$ into Bi$^0$. The latter causes irreversible changes in the morphological structure of the perovskite that can be detected by XRD. The authors observed metallic Bi$^0$ and a shift of 1.4° to a smaller angle in the (0012) plane peak, indicating an increase in the d-spacing due to lithium intercalation (Figure 9D). More studies are needed to fully understand degradation pathways before the enhancement of photobattery stability is possible.

### 3.5 Organic-based photoactive materials

The main advantage of using organic-based materials is being able to tune their physicochemical, optical, and electrical properties through simple synthetic steps. These modifications open up an immense number of possible materials. There are some examples of small organic molecules, polymers, metal–organic framework (MOFs), and covalent organic frameworks (COFs) that have been used in rechargeable batteries [330–333], but not all of them have light absorption and charge storage abilities. Lv et al. reported the first and only COF utilized as a bifunctional electrode to date, in solar rechargeable Li-ion batteries. NT-COF consists of an extended aromatic electron-deficient unit based on 1,4,5,8-naphthalenediimide (NDI) and a triphenylamine (TPA) moiety as an electron-rich unit (Figure 10A) with absorption in the UV region and a broad peak between 450 and 600 nm. It forms a porous 2D trigonal crystalline structure with a hexagonal aperture of 2.4 nm. A 3.65 Å distance was elucidated through XRD for face-to-face π–π stacking of two consecutive planes. Based on these facts, intramolecular charge transfer and
reversible electrochemical reactions required in Li-ion batteries are favorable. The charge and discharge voltage under illumination was 2.53 and 2.96 V respectively at 10 mA g⁻¹, compared to 2.02 and 2.42 V under dark conditions. Therefore, the total battery efficiency was increased up to 117%. Another study showed the utilization of polytrithiophene (pTTh) deposited on carbon paper as photoelectrode in Zn–air batteries [120]. The SEM image in Figure 10B displays the hierarchical spherical structures of 4–5 μm in diameter that are kept together by nanosheets of 20–50 nm in thickness. The rounded structures are beneficial for light capturing and efficiently boost the electrolyte and oxygen diffusion and transport. This has favorable effects on the ORR reaction during the charging process. Although the photoactive material exhibited physicochemical stability over charging and discharging cycles for 64 h without showing any voltage decay, additional efforts are required to increase the photogenerated current.

Zhang et al. also published a pTTh photocathode in a fuel-free photoelectrochemical cell (PEC) with TiO₂ for the water oxidation reaction [334]. This cell produces water and oxygen instead of CO₂ (which makes it environmentally friendly) and electricity concurrently, being the first fuel-free PEC cell reported with these beneficial characteristics. Figure 10C depicts the working principles of the dual-PE PEC cell. It is based on the circulation of OH⁻ and oxygen in alkaline media. When both photoelectrodes are illuminated, the photo-to-electric energy conversion efficiency is 0.18% under air atmosphere and tandem illumination. pTTh PE benefits from the absorption of TiO₂ that blocks the UV light, so it does not reach the organic polymer and thus the photodegradation of pTTh can be avoided completely. pTTh nanostructure on carbon paper is similar to that is described in the previous example, with a 43 μm film thickness.

Lv et al. published a metal–organic polymer (MOP) based on tetraaminobenzoquinone (TABQ) as the organic
Graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) is a metal-free semiconductor first reported by Wang et al. in 2009 as a photocatalyst for H\textsubscript{2} evolution from water splitting [338]. Since then, it has attracted immense attention from the scientific community due to its outstanding characteristics that include facile synthesis from low-cost materials, environmental friendliness, moderate bandgap (~2.7 eV), natural abundance, strong redox capability, high active surface, unique layered structure, and good photo- and physico-chemical stability [339–342]. It consists of tri-s-triazine rings as building units with high nitrogen content and abundant triangular nanopores/defects, which provide a substantial number of active sites for ion adsorption and redox reactions [342, 343]. Its low CB makes it a more suitable photocatalyst in Li–O\textsubscript{2} system compared to TiO\textsubscript{2} or ZnO because it is closer to the redox potential of Li/Li\textsuperscript{+} and its thin layered structure ensures rapid diffusion of oxygen into the electrode. The first publication including g-C\textsubscript{3}N\textsubscript{4} as bifunctional PE was reported by Liu et al. for a photoassisted rechargeable nonaqueous Li–O\textsubscript{2} battery [115]. The simultaneous oxygen electrode and PE is formed by growing g-C\textsubscript{3}N\textsubscript{4} on carbon paper. g-C\textsubscript{3}N\textsubscript{4} acts as a photocatalyst and as an ORR catalyst. Photo-excited holes oxidize I\textsuperscript{−} into I\textsuperscript{3−} ions, which will be reduced back to I\textsuperscript{−} when Li\textsubscript{2}O\textsubscript{2} is oxidized to O\textsubscript{2}. Under illumination, the charging voltage is reduced to 1.9 V, addressing the overpotential issue (4–4.5 V) present in this type of battery (Figure 11A) [54, 344], giving an energy-conversion efficiency of ~140%. Two more publications (one from the same group and the other from Zhuo et al.) using the same PE configuration have been published showing similar results [69, 84]. g-C\textsubscript{3}N\textsubscript{4} forms a uniform and high-density layer on the porous carbon paper electrode (see Figure 11B) and exhibits a clear 2D/2D contact with it, which is beneficial for interfacial electron transfer [340]. This coating structure also provides sufficient space for the deposition of Li\textsubscript{2}O\textsubscript{2} and allows an efficient hole transport from g-C\textsubscript{3}N\textsubscript{4} to I\textsuperscript{−} during the discharge process. Figure 11C and D shows SEM images of the PE surface in photoassisted charging and discharging process. Li\textsubscript{2}O\textsubscript{2} particles are deposited uniformly over the surface of the semiconductor layer during battery discharge, and reversibly decomposed upon photocharging. The stability of g-C\textsubscript{3}N\textsubscript{4} was measured over 70 photo-assisted charge and galvanostatic discharge cycles. No changes were apparent, demonstrating a stable electrode structure and maintenance of almost constant charging and discharging voltages over the cycles.

Another example using g-C\textsubscript{3}N\textsubscript{4} was reported by Zhu et al. In this case, g-C\textsubscript{3}N\textsubscript{4} had nitrogen defects decorated with plasmonic Au NPs [345]. Defects help promote photocatalytic OER reaction by increasing the number of active sites on its surface. Plasmonic Au NPs with an average size of 30 nm reduce electron–hole recombination and, more important, widen the light absorption up to NIR region of the PE [339]. The two-electrode system yielded an energy efficiency of 92.5% after 50 cycles.
mainly attributed to the hot electrons transferred to g-C$_3$N$_4$ from the Au NPs. Podjaski et al. proposed a solar battery half-cell by using semicrystalline 2D carbon nitride as a light harvesting material with the capability of storing electrons for hours in the form of a long-lived photo-reduced state, separating in time the light absorption and catalytic conversion processes [346]. They synthetized a 2D cyanamide (NCN$^-$)-functionalized polyheptazine imide (NCN-PHI) shown in Figure 11E. NCN-PHI is deposited on top of FTO substrate in form of exfoliated nanosheets, yielding a hexagonal pore system nanostructure. The capacity of the NCN-PHI depends on the conjugation length of the imide bridged polymer, which is in turn influenced by the synthetic conditions [347]. The more conjugation it has, the more it can trap electrons on the heptazine rings and delocalize these negative charges across the polymer backbone in the form of stable π-radicals, visible by their blue color [348]. When the holes are extracted to the CE with the help of a redox shuttle having electron donor properties (4-MBA, 4-methylbenzyl alcohol), more electrons can accumulate and reach more negative states. This leads to a more negative open circuit potential and a greater number of electrons stored. The same as g-C$_3$N$_4$, NCN-PHI nanosheets present high electronic stability over 50 cycles, maintaining 75–80% of Coulombic efficiency (Figure 11F). Another important aspect that is involved in the accumulation is their interaction with alkali ions (provided by the electrolyte) that diffuse into and through the structural pores of NCN-PHI.

### 3.7 Other photoactive nanomaterials

Several photoactive materials have been reported over the last years in photo-assisted batteries. For example, Thimappa et al. published a chemically rechargeable photobattery that could be recharged even under ambient light, without applying an external bias. TiN acts as the photoactive material and, KFe[Fe(CN)$_6$] and sodium persulfate (Na$_2$S$_2$O$_8$) as the active species in the battery [349]. TiN is well-known for its broad absorption spectrum up to 650 nm, high electrochemical stability, corrosion resistance and decent conductivity. Oxynitride (TiON) and some traces of TiO$_2$ can be found on the surface of TiN due to oxidation. TiON has light absorption in the visible and UV regions, good conductivity and chemical stability so it contributes positively to the generation of electron–hole pairs and charge separation [350, 351]. Since TiN is not involved in any electrochemical reaction it does not present signs of deterioration over charge–discharge cycles nor gets dissolved in the electrolyte.

Another example is the work published in 2018 by Lv et al. where they synthetized a Ni$_{12}$P$_5$@NCNT (nitrogen-doped carbon nanotubes) catalyst as photoanode in Zn–air photobattery [352]. Ni$_{12}$P$_5$@NCNT forms a p–n heterojunction and when it is exposed to light, photogenerated holes are transferred to Ni$_{12}$P$_5$ surface to oxidize water and the electrons move to the NCNT surface to reduce oxygen. The bamboo-like CNTs are decorated with Ni$_{12}$P$_5$ NPs that are highly dispersed (Figure 12A and B). CNTs construct 3D
networks that are greatly favorable for fast electrons transfer and help to prevent aggregation of Ni$_{12}$P$_5$ NPs [353]. Brunauer–Emmett–Teller (BET) analysis displayed a hysteresis loop distinctive of a mesoporous material with a surface area of 120.3 m$^2$ g$^{-1}$ and an average pore size of ~3.6 nm. This proves that the active sites are sufficiently exposed to the electrolyte to promote the photocatalytic reactions [354]. The Ni$^{3+}$ peak at 853.8 eV in high-resolution XPS analysis was red-shifted compared to the peak for Ni$_{12}$P$_5$ NPs alone (852.6 eV) [355]. This demonstrates the strong coupling effect between NCNT and Ni$_{12}$P$_5$ NPs, which facilitates the electron transfer to Ni$_{12}$P$_5$ NPs. However, the round-trip efficiency obtained was only 64.2%. In 2020, Song et al. published an all-solid-state Li–air photobattery that can operate at a very low temperature (~73 °C) [356]. The working mechanism involves the deposition of a very thin layer of Ru NPs (5–20 nm in size) with surface plasmon resonance properties, as Figure 12C and D demonstrates. The photogenerated carriers formed at the electrode release the energy in form of heat dissipation, resulting in light-induced thermal heating of the battery, increasing the charge storage and cycling life [357, 358].

Two graphitic-like nanomaterials were reported for Li–CO$_2$ batteries. The first consisted of a hybrid photocathode employing SiC grown on rGO (SiC/rGO) [68], where SiC was synthesized in situ on the rGO surface. They adopted “island-in-sea-like” morphology (see Figure 12E) with cubic structured crystals. The CO$_2$ adsorption is favored by 2D nanosheets rGO as well as the Si–OH bonds present on the surface of SiC. The photoelectrode remains stable over 20 cycles, maintaining its initial morphology. In 2021, 3-nanosheet thick ultralarge size siloxene (2.05 nm) was proposed as a photoactive material with energy storing properties by C. Jia et al. [67]. It confers an impressive discharge/charge voltage retention (98 and 93% respectively), round-trip efficiency of 185% in the first cycle that remained at 170% after 100 cycles. Figure 12F shows siloxene nanosheets with a graphene-like structure formed by S$_6$ rings connected by Si–O–Si bridges with surface-terminated functional groups such as –O, –H and –OH, corresponding to the Kautsky structure [359, 360]. Its structure, optical bandgap of 2.48 eV, high surface area and low recombination rate allow high photocatalytic activity yielding an impressive discharge capacity of 1170 mA h g$^{-1}$ after 12 h of illumination (at 0.75 mA cm$^{-2}$). The formation of Li$_2$O$_2$ was fully reversible, demonstrating great stability of the PE. Materials with 2D nanosheet morphology (such as SiC, siloxane, g-C$_3$N$_4$, and Cs$_3$Bi$_2$I$_9$ nanosheets) have proven to yield higher capacity values due to the high electrolyte insertion in their structure [361].

4 Challenges and outlook

Currently, photo-rechargeable batteries are still in an early experimental stage, presenting numerous problems and challenges. The maximum overall efficiency in a two-electrode photobattery achieved to date was 9% (see Table 2, where a summary with all the photoactive...
nanomaterials and their performance is described). Based on these values, we can conclude that the commercialization of integrated photobatteries remains feasible but not in their current state. In this section, we present the main challenges standing in the way of developing efficient PEs. Insights into the most efficient nanomaterials will be offered for developing ideas in the future rational design of PEs (Figure 13).

Low efficiencies of PBATs are due to a variety of factors including low light absorption of nanomaterials, high charge recombination within the photoactive material and/or heterojunctions, low storage capacity and cycle reversibility. The energy levels of the photoactive material must allow broad absorption in the visible range of the spectra and overcome the energy barrier for efficient photocharging in the absence of an external energy supply. However, this remains a challenge due to large overpotentials required by metal anodes, especially in Li-based batteries. Charge recombination can be diminished by rationally designing heterojunctions or nanostructures that enhance charge transfer within and among them. The storage capability and cycle reversibility depend on the nanomaterial’s nature and the working principles of the PBAT; and will be discussed later in this section. In some metal-ion batteries, the charge is stored by means of ion intercalation with a host. The limitation comes from the intrinsic diffusivity of the metal ion in the solid PE, which inhibits the intercalation/deintercalation rate and extends the charge/discharge processes. Because of their small size and shape, nanomaterials allow for a higher degree of metal insertion/removal due to the shorter diffusion distances for metal ions within the particles. Despite this, distortion of the crystal structure and volume expansion upon intercalation can be irreversible, causing deep cracks and exfoliation/pulverization of the photoelectrode. For bifunctional PEs, n-type semiconductors are preferred because they can accumulate electrons in the CB effectively, counterbalancing the positive charge due to metal ion insertion. However, Lou et al. demonstrated that p-type semiconductors (such as MoO3) can also efficiently harvest light and store energy by Na+ intercalation [248], opening new possibilities. Surface modification of the active materials with electron-rich groups can effectively decrease the metal ion insertion energy barrier by increasing the interaction with metal ions and active sites. Transition metal compounds from IV.B and V.B groups are well-known to intercalate with metal ions efficiently [102, 220]. Perovskite-based nanomaterials have shown great ion intercalation capabilities as well, but more investigation is required to understand degradation mechanisms and enhance long-term stability [107, 363–365].

Corrosion of the PE usually arises from redox reactions with the active species in the electrolyte. PBATs suffer greatly from corrosion and passivation due to the formation of a SEI (i.e., Li2O2) that is not reversibly dissolved and accumulates in the electrode surface, hindering the light-absorption and diminishing the electrode–electrolyte contact [37, 366]. In addition, parasitic reactions on the metal electrode surface might occur because of light-induced decomposition of the electrode. Dissolution of nanomaterials, such as BiVO4 or MoO3 also represents a critical drawback and compromises the long-term stability of the battery. The compatibility of electrode materials and redox active species along with the solvent should be evaluated in advance to ensure the stability of the device. Photoinduced corrosion is another commonly found issue in some organic materials, like pTTh, Cu2O [367], or metal chalcogenides, such as CdS. It leads to an important loss in photogenerated current and Coulombic efficiency [368, 369]. For organic materials, the photodegradation is related to changes in the conjugated molecular structure. In the specific case of CdS or other chalcogenide-based nanomaterials, photogenerated holes are transported to the surface where they irreversibly promote the oxidation of S2− ions into sulfur (S0) and/or sulfate (SO42−) [368]. The stability and reliability of the PBATs highly depends on the lifetime of the photoactive material or photocatalyst. One possible solution is to introduce a hole scavenger in the electrolyte that prevents oxidation of the semiconductor by the photogenerated holes [280]. Another

Figure 13: Schematic diagram summarizing the main contents of this review, i.e., main groups of nanomaterials that are used as PE in PBATs. Copyright 2021, American Chemical Society and 2016, Royal Society of Chemistry.
Table 2: Classification and main characteristics of described two-electrode integrated photo-rechargeable batteries.

<table>
<thead>
<tr>
<th>Photoanode active material</th>
<th>Photocathode active material</th>
<th>Type of integrated photobattery</th>
<th>Capacity (mA h g⁻¹)</th>
<th>Cycling number</th>
<th>η_{Conversion} (%)</th>
<th>η_{Battery} (%)</th>
<th>Need of external bias</th>
<th>Reference</th>
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<td>SFB</td>
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<td>4</td>
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<td>906</td>
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<td>–</td>
<td>–</td>
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<td>[133]</td>
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<td>–</td>
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<td>Co-TABQ nanosheets</td>
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<td>50</td>
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<td>12</td>
<td>–</td>
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strategy involves coating the nanomaterials with a thin anti-photocorrosion layer to form heterojunction or core@shell structures, such as CdS@ZnS QDs [370]. The difficulty of this option lies in finding a highly conductive material, with high charge transfer, which however does not affect the light-harvesting and storing properties of the PE.

From a morphological point of view, nanotubes, nanowires, or nanorods are more beneficial compared to other NPs since they exhibit higher reversibility of intercalation and have enhanced specific surface area. These types of nanostructures are also beneficial because of their expansive surface area that allows more active sites to be in contact with the electrolyte and/or the active species. In addition, the increase in the surface area has a positive impact on light absorption, which can increase IPCE [168, 371, 372]. Nanorods and nanowires are more photoactive and transport charge carriers more effectively compared to nanospheres, as a result of their lower coordination number [377]. In general, these 1D nanostructures provide rapid diffusion of charges (e.g. for TiO$_2$ nanostructures it is around 200 times higher [378]) which leads to low recombination rates. Well-aligned or vertically oriented nanostructures are recommended for an optimal charge and ion transport efficiency since charge transport is preferred in one distinct direction, which decreases even more charge recombination. Another advantage of using 1D nanostructures is the formation of a packed interconnected network [379, 380] that was shown to improve electronic conductivity and considerably prolonged lifetime due to having a reduced number of agglomeration sites [381].

Mesoporous materials have also benefited from more rapid intercalation/deintercalation of ions, enabling them to store more energy compared to their bulk counterparts. The thin mesoporous walls confirm short diffusion paths for ion intercalation and charge transfer. Such materials are composed of micrometer-sized particles with pore size of 2–50 nm [60]. Because of their uniform and ordered porosity microstructure, the internal pores are also in contact with the electrolyte, ensuring a high surface area in contact with the photoelectrode. As a result, mesoporous materials have been found to have superior cycling capability for Li-ion batteries [382–384]. Hole-electron recombination decreases when crystallinity increases, influencing the photogenerated current within the device. Regardless, the electrochemical properties and the rate performance need to be improved for most nanomaterials. It is highly recommended to combine different nanostructures to form heterojunctions or nanocomposites that can compensate the individual flows of each material or synergistically help improve their properties. Heterojunctions and nanocomposites also promote electrolyte diffusion, charge separation, and ion transfer, improving electrochemical kinetics [151]. In addition, the exploration of different synthetic procedures might improve the optical

<table>
<thead>
<tr>
<th>Photoanode active material</th>
<th>Photocathode active material</th>
<th>Type of integrated photobattery</th>
<th>Capacity (mA h g$^{-1}$)</th>
<th>Cycling number</th>
<th>$\eta_{\text{conversion}}$ (%)</th>
<th>$\eta_{\text{battery}}$ (%)</th>
<th>Need of external bias</th>
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<td>[67]</td>
</tr>
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*At 655 nm illumination. **At 1 sun illumination. ***At –73 °C.
and electrochemical properties of the nanomaterials by having good control over the defects and morphology. For instance, annealing precursors that emit gases (e.g. CO₂) will tend to increase the porosity of the nanostructure. Ball-milling techniques are also recommended to increase the surface area, hence, the photocatalytic activity. Electrodes are the most expensive component of batteries, and the nanomaterials synthesis increases the cost even further. For this reason, it is mandatory to seek out novel low-cost nanomaterials or new preparation techniques including ball milling or liquid-based methods which are convenient for scaling-up commercial-sized batches. The use of plasmonic NPs helps increase light-absorption into NIR region. In general, 2D materials shorten the charge diffusion path during charge and discharge and they are suitable host materials to form heterojunctions and composites. The size and shape of the pores in 2D nanosheet-based PE materials are also critical factors that control the penetration of the electrolyte, which will influence the overall specific capacity and the charge/discharge rate capability [385, 386]. 2D materials also benefit from high surface area. As a result, they have a large number of exposed active sites that boost the electrochemical kinetics and conductivity of the PE. However, an increase of the surface area does not always mean an improvement on the performance due to the possible excessive formation of SEI layer in the surface of the PE [361, 387].

As it can be observed from the main limitations, there are still many factors that hinder high battery stability and reliability, hence, performance. Nanomaterials with high surface area and small size showed higher performance due to the increase in surface-to-volume proportion, which extend the number of active sites, interfacial charge transfer, and improve reaction kinetics with redox active species, which will enhance the catalytic activity. In this way, single atom catalysts are the direction to follow. These individual metal atoms on support materials benefit from a low coordination environment (allowing a higher interaction), quantum size effects, homogeneity of active sites, and metal–support interactions which improve charge transfer [388–390]. Having this said, durability issue needs to be addressed for this type of highly active catalysts. We would like to point out the importance of integrating researchers from a wide variety of backgrounds (such as Chemistry, Physics, Engineering, and Material Science) to work together in overcoming these limitations. Additionally, an emphasis should be given to life cycle analysis, to better assess the economic, environmental and social impacts associated with all the stages of the life cycle and components of PBATs [391, 392]. This includes the resources generation, material processing of all battery components, product manufacturing, package and distribution, use and end of life.

One critical aspect we would like to mention is the necessity of standardization of experimental conditions and characterization tests in the field of PBATs. Currently, it is very difficult to directly compare results and draw conclusions from the published literature. Without such standardization, progress cannot be guided in a rational way. Furthermore, photo-to-electric energy conversion efficiencies are not discussed in most publications on photorechargeable batteries. There has been a proposed guideline for Li-ion batteries that can be adapted for other fields or types of batteries [393]. For PBATs, it should include photo-to-electric energy efficiency, round-trip efficiency, charge and discharge capacity (or areal capacity) at a specific charging-rate, and charge and discharge voltage, among others. Nanomaterials tested in half-cells should also demonstrate their performance in a full cell.

Lastly, an emphasis on in-depth theoretical research focusing on voltage, current, energy and power matching of the different components of the storage system would prove beneficial to the field. This could allow for predictive studies of photobattery performance and rational design of devices.

5 Conclusions

To summarize, we believe that nanomaterials are the key to meaningful progress in photoelectrode research for solar rechargeable batteries. Their significance was demonstrated through relevant examples discussed in this review and their main advantages have been discussed compared to bulk materials. Future generations of photobatteries with high energy and photo-to-electric efficiency will assuredly rely on nanostructured materials. Although fabrication of a low-cost stable and efficient photoelectrode remains a challenge, projected growth in the field will eventually lead to a solution for viable commercialization. In particular, the price of Li-ion batteries will drop below $100 and lithium–nickel–manganese–cobalt-oxide (NMC)–graphite–silicon and LFP–graphite will dominate the market in the next 20 years. The integration of the photo battery in these two systems will reduce range anxiety and increase the calendar life of the photobattery. We expect important developments of these integrated systems help meet environmental and energy goals in the coming decade.

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