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Critical review on storage of solar energy in the rechargeable batteries

R.Nagaraju[1], V.S Vani[2], M Ramesh Kumar[2], Dr. S. Venkateswara Rao[3]

[1&2]Department of Physics, Holy Mary Institute of Technology & Science, Hyderabad, Telangana-501301 (India).

[3]Department of Physics, JNTUH College of Engineering (Autonomous), Hyderabad, Telangana-500072 (India).

ABSTRACT

The Study of imparting the solar energy into the rechargeable battery provides a solution to achieve clean energy charging, especially the simplified solar powered rechargeable batteries. This concept has been demonstrated the employment of high efficiency nano photo catalysts for capturing solar energy into batteries. In this review, author gives a brief analysis on the conventional applications of solar energy, and systematically discusses the new type applications for rechargeable batteries. The development of solar powered rechargeable batteries would greatly contribute to building new resource conserving society.

Keywords: Nano photo catalysts, Solar rechargeable batteries, Solar energy storage photo electrode.

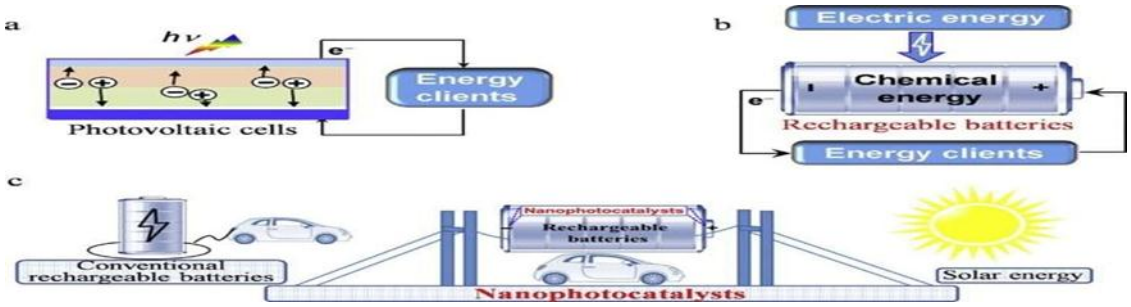
INTRODUCTION

With the growing energy recruitment and environmental crisis, development and application of renewable energy have become a matter of great urgency. Solar energy, one of promising renewable energy, owns the abundant storage around 23000 TW year-1 (Terawatt (TW) is equal to one trillion (1012) watts. The total power used by humans worldwide is commonly measured in terawatts) and could completely satisfy the global energy consumption (about 16 TW year-1) [1, 2]. The nonpolluting source and low running costs endow with very large application prospect. However, the intermittency inherently hinders its widespread applications, and this short coming simultaneously plagues other kinds of renewable energies. Consequently, it is important to search for energy conversion/storage systems to balance the mismatch between production and consumption.

The common photovoltaic cells only convert solar energy into electric energy for the straight usage to energy clients, without the enduringly stored function (Fig. 1a). While the rechargeable batteries enable to convert electric energy into the storable chemical energy and the realize the recyclable conversion/storage between electric energy and chemical energy (Fig. 1b). Besides, the rechargeable with the high energy density, have been widely applied into the various fields such as portable electronic equipment, electrical vehicles, aerospace and other important areas [3-6]. Therefore, the exploitation of solar energy in rechargeable batteries could not only achieve the large- scale application of solar energy, but also assist the conventional rechargeable batteries in saving the input electric energy. For the in-depth development of the solar energy storage in rechargeable batteries, the photo catalyst is a pivotal component due to its unique property of capturing the solar radiation, and plays a crucial role as a bridge to realize the conversion/storage of solar energy into rechargeable batteries (Fig. 1c). Based on the Nano scale superiority, the Nano photo catalysts have been extensively applied in some conventional fields such as photo electrochemical water splitting decomposition of

Author for correspondence:
Department of Physics, Holy Mary Institute of Technology & Science, Hyderabad, Telangana-501301 (India).

organic pollutants and energy harvesting devices and so on [7-9]. Besides, the solar energy storage in rechargeable batteries is an emerging solution to revolutionize the photo electricity conversion, further highlights the significance of nano photo catalysts. Compared with the external combination of photovoltaic cells, the solar powered rechargeable batteries which integrate photo electrodes and rechargeable batteries into a single device further simplify the entire systems [10-12]. In the year 1976 the first photo rechargeable battery investigated a photo reaction on a semiconductor silicon/silicon oxide (P-IaSi/SiOx) electrode using silver iodide tungstate(Ag6I4WO4) in 1990 [13, 14]. However, recently, the increasing studies and reports have focused on the direct integration of photo-electrodes into the rechargeable batteries such as Li-ion batteries, Li-O2 batteries and redox flow batteries [15–17]. These systems possess simplified device configuration and enhanced energy density. Therefore, this incorporative strategy has become an alternative avenue for realizing the low cost and high performance solar powered rechargeable batteries. In this review, we generalize the characteristics of Nano photo catalysts and recent progress of solar energy on the conventional area, and then provide a comprehensive understanding for the new application of solar energy in rechargeable batteries from two aspects, the external combination of photovoltaic cells and the internal integration of photo electrodes with rechargeable batteries. Under consideration of the various systems in rechargeable batteries, recent advances on the solar powered rechargeable batteries will be systematically summarized and discussed based on the various systems of the solar energy storage in the Li-I batteries, Li-O2 batteries, Li-S batteries, dual-liquid redox batteries and other batteries. Finally, we also propose the challenge and outlook for solar powered rechargeable battery as a competitive and innovative strategy for future large-scale energy applications.



ʿFig.1.The energy storage mechanisms of photovoltaic cells (a) and (b) rechargeable batteries and (c) Significance of nano photo catalysts on the combination of the rechargeable batteries and solar energy.

Solar systems with energy storage are surging in popularity for a few reasons. The cost of solar batteries is decreasing; meanwhile, the prevalence of grid outages has climbed. There was a 30 percent increase in grid outages between 2009 and 2019, with a total of 37 million people affected in 2019. Blackouts can cause property damage, including frozen pipes and flooded basements. Hundreds of thousands of customers lost power in Wisconsin and Dallas County in 2019 due to severe thunderstorms, resulting in millions of dollars of damage. In California, intentional blackouts have been utilized to prevent wildfires. "While California has always led the country in solar deployment, the drivers behind that growth have shifted," said Austin Perea, a senior solar analyst for Wood Mackenzie. "This is primarily due to new-build solar demand and increased consumer interest in solar + storage solutions as a result of public safety power shutoffs that have left hundreds of thousands of utility customers in the dark."

Convention applications of solar energy

It is necessary to in-depth understand the characteristics and conventional applications of

Nano photo catalysts, prior to referring to the applications of solar energy in rechargeable batteries and other new domains. The photo catalyst used in the photo catalyst to promote the photochemical reaction. Based on the phase types of photo catalyst and reactants in photo catalysis, the photo catalysts can be categorized into two types: Homogeneous photo catalysts and Heterogeneous photo catalysts [18, 19]. In Homogeneous photo catalysts, the reactants and photo catalysis exist in the same phase, and the commonly used Homogeneous photo catalysts involve ozone and Photo Fenton systems. On the contrary, the catalysts exhibit the different phase with the reactants in heterogeneous photo catalysis, and the common photo catalysts mainly include the transition metal oxides and semiconductors. The semiconductor photo catalysts with inconsecutive energy bands have the typical photo excited state feature. After semiconductor absorbs light irradiation, the electrons in the valence band of the photo catalysts are excited to the conduction band (CB), while the holes are left in the valence band (VB) (Fig.2a). The band gap between the top of VB to the bottom of CB, is responsible for the absorbed region of solar spectrum. For instance, Fe2O3, Cu2O, C3N4 and GaP are the representative photo catalysts driven by visible light, which account for more than 40% of sunlight, from400nm (3.12eV) to 800 nm (1.56eV) (Fig. 2b) [21]. Inspired by the significant finding on TiO2 photo catalysis by Honda Fujishima effect in 1967 [22], various nanophotocatalysts have been exploited and utilized for solving the contemporary issues such as the photo catalytic water splitting, organic contaminant decomposition, energy harvesting devices and decomposition of crude oil (Fig. 2c) [23-26]. Used TiO2 nanoparticles as photo anode and constructed a solar storable fuel cell with efficient photo degradation of organic contaminants in waste water for direct electricity generation (Fig. 2c) and this cell delivered a stable voltage of 0.6 V at a constant current of 20 μA cm-2 , the common photo voltaic cell is a kind of electrical devices that directly converts the solar energy into electricity by the photovoltaic effect, and the complete of Nano photo catalysts have been widely used in photovoltaic cells(PVs), such as the Si-based solar cells, perovskite solar cells (PSVs) and dye sensitized solar cells (DSSCs). The following section reviews the recent progress on the above mentioned applications.

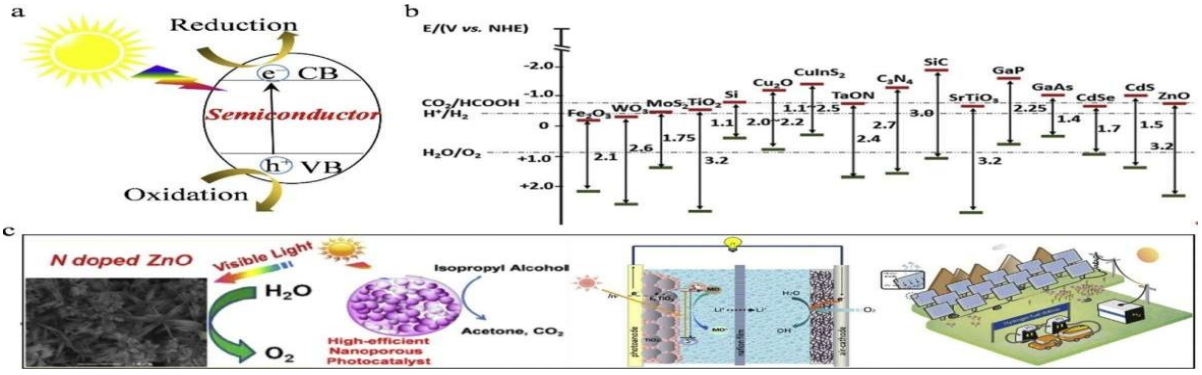


Fig.2. (a) The working mechanism of semiconductor photo catalysts. (b) The conduction band (red line) and valence band (green line) positions of the reported photo catalysts (V vs. NHE, pH=7).

Photo catalytic water splitting

Water splitting contains both Hydrogen evolution reaction (HER) and Oxygen evolution reaction (OER). Because the Oxygen evolution reaction involves multiple electron transfer and there by suffer from sluggish kinetics, the achievement of an efficient OER is significantly more challenging than that of HER. Two of the mainly research directions in realizing photo catalytic water splitting are the acquisition of photo catalysts with high catalytic activity and the use of earth abundant elements for the fabrication of inexpensive photo catalysts. The distinctions of various nano photo catalysts with controlled morphologies including one-Dimensional Nano

structures, facet controlled semiconductor materials and hierarchical composite nano structures, and pointed out the significance of high quantum yield [27]. In the case of pure water photo catalytic splitting the highest quantum yield thus far is 56% , reported for La-doped NaTaO3 under UV irradiation(h=270 nm) [28]. Besides, an extremely high quantum yield of nearly 90%under visible light (h=420 nm) was found using Ag3PO4 for the evolution of O2 in water photolysis [29]. The advantages of 2D nano scale materials in photo catalytic areas and highlighted hetero junction architect × tures based on inter facial engineering at the nano scale and energy diagram alignment of 2D material, which were expected to further facilitate charge separation and transport along with enhanced photo catalytic performance [30]. The influence of crystal growth, doping and here to structuring on the TiO2 based photo catalysts with unique and properties [31]. In practical, the most efficient OER catalysts in acidic or alkaline solutions are noble metal based catalysts such as IrO2 and RuO2, but they suffer from the advantages of high cost and scarcity. Therefore, it is requisite to explore photo catalysts with low cost and high performance, and the transition metal Mn-, Co-, and Ni-based oxides and carbon nitride are fortunately emerging as the potential candidates. The man-size λ-MnO2 obtained from the nano crystalline LiMn2O4, and showed a significantly higher water oxidation catalytic activity than that with micrometer and irregular particle sizes [32]. In contrast, polymorph LiCoO2 can hardly catalyze the water splitter reaction [33]. Furthermore, the low cost carbon nitride nano sheets have showed the great potential in the photo catalytic hydrogen evolution by the visible-light-driven, such as the grapheme like carbon nitride nano sheets and vanadate quantum dots/graphitic carbon nitride Nano sheets and so on [34].

Organic contaminant decomposition

The self-decomposition of organic contaminants at room temperature the self-decomposition of kinetically slow, While the employment of the e- -h+ pairs from motivated nano photo catalysts is conductive to accelerate degradation ability. The typical working mechanism is shown in the following process:

$E=h\nu \rightarrow$ photo catalyst $\rightarrow e^- + h^+$

Org + $h^+ \rightarrow CO_2 + H_2O$ + other products (on VB)

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ (on CB)

Under light irradiation, the excited h+ from photo catalysts can oxidize surface absorbed H2O to form •OH radicals which could attack organic contaminants or directly oxidize organic molecules. At the same time, the excited e- can react with O2-to yield superoxide radical anions •O2- species. For example, a nonporous SrTiO3 photo catalyst by a nano template assisted sol gel hydrothermal technique, and this particular nonporous attained a great enhancement in photo catalytic efficiency by eliminating isopropyl alcohol(IPA) degradation into acetone and CO2 (24). Ag3PO4Photo catalyst shows larger quantum yields compared with the well-known oxidation photo catalysts such as TiO2, BiVO4, and WO3. The organic decomposition o−f Ag3PO4-based nanophotocatalysts and suggested that the faceted crystals induced high activity due to preferential charge transfer to septic crystal planes [35]. Note that the surface Plasmon resonance effect of Ag nano particle in this type nano photo catalysts is still a vital issue needed to be further improved.

Solar battery prices are falling

Solar energy is an intermittent energy source. This means that solar panels produce power when the sun is shining and not when it is’nt. Energy storage allows the solar system to supply power when the sun has set or in cloudy weather, expanding the capabilities of solar energy systems. There are two main types of solar batteries: lead-acid batteries (like you have in your car) and lithium-ion batteries. The latter is far more advanced, longer-lasting, and requires less maintenance. Not surprising, lithium-ion batteries have a higher upfront cost, but the price has been decreasing significantly in recent years. The cost of lithium-ion battery storage fell 35 percent from the first half of 2018 to now (December 2019) and 76 percent since 2012. This downward price trend is good news for renewable solar energy in 2020 and it’s likely to continue. Natural gas plants are often used to meet peak energy loads because they can more easily be turned on and off than coal or

nuclear power plants. Lower costs make it easier for intermittent renewable energy sources such as wind and solar to be cost-competitive with dispatch able fossil-fired power plants. Price decreases in utility-scale battery banks now make solar plus energy storage competitive in many areas on price alone. Battery banks can make it unnecessary to fire up power plants during times of peak demand, reducing fossil fuel consumption. The greater the capabilities of solar, the less attractive and financially viable these speaker power plants become. On the residential side, more homeowners are relying on solar systems with battery storage for emergency power during grid outages than ever before. This is an especially attractive option in areas prone to extended power outages due to natural disasters or with inadequate utility infrastructure, like Puerto Rico.

Federal solar tax credit starts decreasing

A tax credit is a dollar-for-dollar decrease in taxes owed to the federal government. A tax credit is more valuable to the taxpayer than a write-off. The solar Investment Tax Credit (ITC) is a valuable incentive by the federal government that reduces the total cost of going solar. The solar credit was not extended by Congress, so it will be tapering down each year, starting in 2020. This means that the incentive will be greater in 2020 than in subsequent years. Currently, the credit is set at 30 percent, but starting in 2020, the solar ITC will be worth 26 percent of the total solar system cost including installation. In 2020, a $10,000 solar system will qualify for a $2,600 tax credit. In 2021, the same system will qualify for a $2,200 tax credit. The solar ITC will continue to decrease "indefinitely to 10% for commercial and utility solar projects, and zero for residential."

Electric vehicles boost electricity demand

Surprisingly, electricity demand in most advanced economies has leveled or even decreased in recent years. However, global electric vehicle sales are expected to reach 11 million units in 2020 and then surge to 97 million vehicles in 2025. And these vehicles require electricity to power them. According to the National Renewable Energy Labs, electric vehicles could cause a 38 percent increase in U.S. electricity demand. An increase in peak energy demand will create a shift in the energy market, boosting the demand for new power generation. Renewable energy sources, like solar, may help meet that demand. Because many electric vehicle owners are eco-minded, many are installing solar systems so their cars can run off of 100 percent renewable energy. In fact, many solar installation companies also install electric vehicle chargers and this trend is growing.

Applications of solar energy in rechargeable batteries

Nanophotocatalysts relied on the excited e− -h+ pairs upon absorbing the light irradiation also have been extensively investigated in the areas of photo electrochemical reduction of carbon dioxide, decomposition of crude oil and so on. TiO2 and ZnO nanoparticles have also been adopted for the photo catalytic degradation of diesel oil and crude oil [36, 37]. And this process has become an innovative idea that can be implemented in future environmental usage. According to above discussions for the conventional applications of solar energy, it can be found that the nanophotocatalysts present the different photo catalytic activities in diverse systems due to the distinct energy levels of CB/VB, band gap and concentration ration of excited e− and h+ under the illumination (for instance, n type and p type semiconductors). Classification and characteristics of common photo-catalysts have been summarized in Table 1.The photo-catalysts indeed play a vital role for capturing the solar energy, so that these typical characteristics and conventional applications of photo-catalysts have the reference significance in the new- type solar rechargeable batteries. Considering the redox process of electrode materials during the "rocking-chair" working of rechargeable batteries, the feasibility of solar rechargeable batteries by employing photo catalysts needs to satisfy many factors, including the following points:

1. The matching of potential energy-levels between the photo catalysts and rechargeable batteries
2. Reasonable usage of excited e− and h+ of photo catalysts in rechargeable batteries)
3. Photo catalytic activities, photoelectric conversion and storage efficiency, side

reactions of photo catalysts in various systems of rechargeable batteries.

Therefore, the link of photo catalysts into rechargeable batteries will need the highly compatible co-ordination from the materials characteristics and working principle, there are the great challenges in the septic solar rechargeable batteries [38, 39]. Rechargeable batteries have been developed as the one of most efficient systems for the electrical energy storage, which are extensively used in modern society due to the increasing electric requirements. Different from the PVs with the only conversion function, the rechargeable batteries are based on the energy conversion and storage between electrical energy and chemical energy. Harvesting solar energy into high-performance rechargeable batteries could not only achieve the large-scale utilizations of solar energy, but also short the path from renewable energy to electric energy. The highly effective, long-durable, less-expensive and environmentally-friendly incorporation of solar energy into various batteries.

External combination of PVs into rechargeable batteries

It is well known that the photovoltaic cells (PVs) have been considered as one kind of the fastest growing renewable energy technologies. However, the intermittency of PVs output power has been a major shortcoming owing (as a result of) to its direct coupling to the availability of the solar irradiance. Rechargeable batteries have the merits of the continuous and long-term charge/discharge, especially for some commercialized Li-ion batteries. (Fig.3a).Solar photovoltaic (PV) charging of Li-ion battery by externally wiring the high-effective silicon PV modules into the iron phosphate type Li-ion cell [40]. The assembled system could be charged at a rate of up to 1.5C with an average voltage of 3.37 V (full charge in about 40 min) and the optimized solar charging system efficiency reached 14.5%, by combining a 15% PV system solar to electrical efficiency and a nearly 100% electrical to battery charge efficiency (Fig. 3b). It is noteworthy that as battery voltage passing the PV maximum power point, the rapid drop of power could significantly reduces the risk of thermal damage to battery systems during charging. The use of perovskite solar cell packs with four single CH3NH3PbI3 based solar cells connected in series for direct photo-charging lithium-ion batteries assembled with a Li4Ti5O12 anode and a LiFe PO4 cathode. The photo-electric conversion and storage efficiency is about 7.36% at 0.5C, moreover the discharging capacity decreased from 141 mAhg−1 to 111.6 mAhg−1 after10 cycles (Fig. 3c) [41]. In order to further enhance photo-electric conversion and storage efficiency, an ultralow power direct current-direct current (DC–DC) boost converter into the perovskite solar cells (PSC) for photo charging a Li4Ti5O12-LiCoO2 battery (Fig. 3d). This approach leads to a high overall efficiency of 9.36% and average storage efficiency of 77.2% at 0.5C. In addition, the discharging capacity undergoes a degradation from 151.3 mAh g−1 to 134.4 mAh g−1 after 10 cycles (Fig. 3e) [41].

Table 1 Classification and characteristics of the common photo-catalysts.

Type	Photo catalysts	Band gap	Absorbed spectra	Conventional applications	Ref.
	TiO2		UV light	Dye sensitized solar cells	[21]
				Photo catalytic water splitti3n.g0 eV (rutile) 3.2 eV (anatase)	[25,26]
				Decomposition of crude oil and diesel oil	[31]
				Photo electrochemical reduction of carbon dioxide	
				A solar storable fuel cell with	[37]

				photo-degradation of organic waste	
	ZnO	3.2 eV	UV light	Photo catalytic water oxidation	[23]
				Photo degradation of ethylene blue	[30]
N type				Photo degradation of diesel crude oil	[36]
	C3N4	2.7 eV	Visible light	OH radical generation	[34]
				Photo catalytic hydrogen evolution	
				Photo electrochemical reduction of carbon dioxide	
	Fe2O3	2.1 eV	Visible light	Photo degradation of phenol and RhB	[30]
				Photo electrochemical water splitting	
	La-doped NaTaO3	0.09 eV	UV light	Photo catalytic water splitting	[28]
	Ag3PO4	2.36 eV	Visible light	Water photo oxidation	[29]
				Photo catalytic decomposition of organic contaminants	[35]
	CdS SrTiO3	1.5 eV	Visible light UV	Photo catalytic reduction of Cr(VI)	[30]
		3.2 eV	light	Degradation of organic pollutant	[21]
				Photo electrochemical reduction of carbon dioxide	[24]
	P-Si	1.1 eV	Visible light	Si-based solar cells	[13]
				Photo electrochemical reduction of carbon dioxide	[21]
	GaAs	1.4 eV	Visible light	Photo electrochemical reduction of carbon dioxide	[21]
P type	Cu2O	2.0~2.2 eV	Visible light	Photo electrochemical reduction of carbon dioxide	[21]
		2.25 eV	Visible light	Photo electrochemical reduction of carbon dioxide	[21]

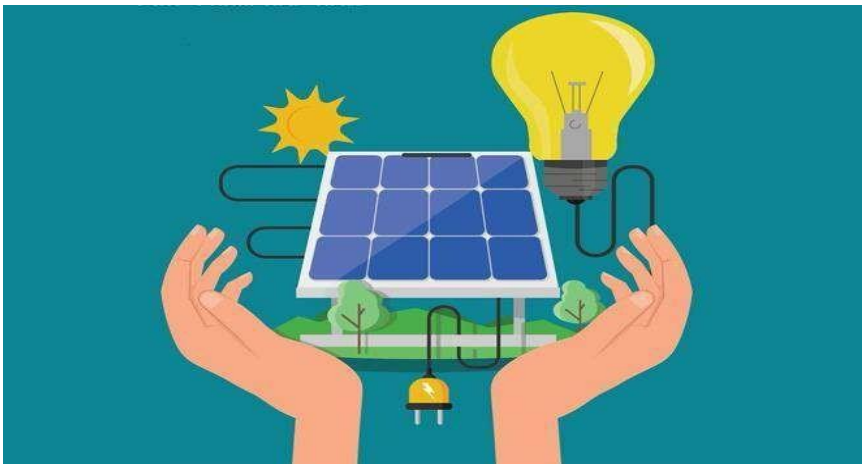


Fig.3. (a) External photovoltaic cells into rechargeable batteries.(b) Silicon based solar charging of a 15-cell lithium-ion battery module-voltage per cell, current, charge rate, and battery charge capacity as a function of time.(c) Overall photo-electric conversion efficiency of the PSCs-LIB device (η2). (d) Photo charging plots of Li4Ti5 O12-LiCoO2 cell using by DC–DC booster and corresponding cycling performance. (e) Overall efficiency of PSCs-DSC Charged Li-Ion cell.

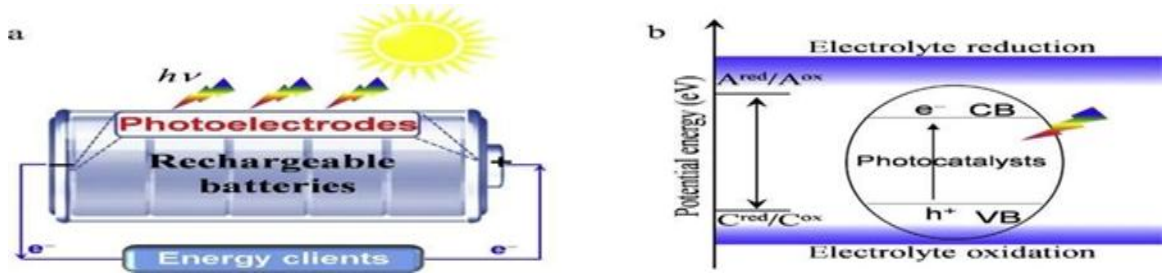


Fig.4. (a) Schematic diagram of the internal integration photo electrodes into rechargeable batteries. (b) Potential energy of the three considerable sections including the anode and cathode of rechargeable batteries, CB and VB of photo-catalysts, and reduction and oxidation of electrolyte.

Internal integration of photo electrodes into rechargeable batteries

To simplify the storage process of solar energy in the form of electricity, a reliable and promising strategy is the internal integration of photo electrodes into rechargeable batteries (Fig. 4a). The conventional rechargeable batteries mainly consist of the anode, cathode, separator and electrolyte and can be segmented into the organic, the various types of the usable active materials, the electrodes of rechargeable batteries involve the solid, gas and liquid three types. Therefore, the internal integration of photo electrodes into rechargeable batteries will need the highly compatible co-ordination based on the potential energy of each part for importing the high-effective electric energy (Fig.4b). A variety of integrated solar batteries have been developed as shown in Table2.The recent progress could be summarized and discussed from some representative directions such as the solar energy storage in Li-ion batteries, Li-O2 batteries, Li-sulfur batteries, Li-iodine batteries, dual-liquid redox batteries and other batteries.

Solar energy storage in Li-ion batteries with solid cathode

The rechargeable battery technology has begun to be the commercial productions around solid-electrode-based Li- ion batteries with suitable energy densities, and the commercial materials have covered the Li4Ti5O12, LiCoO2, LiFePO4

and LiMn2O4 and so on. These Li-ion batteries have been broadly employed in electric powered equipment whereas their high safety, applicable cost and long cycle durability have raised the total charge of electronics. The compatible strategies on the direct conversion of solar energy into the solid-cathode based Li-ion batteries will speed up the commercialization and industrialization of solar energy in rechargeable batteries. A new integrated power pack consisting of a DSSC and a LIB was fabricated based on double-sided TiO2 nano tubes anode (left of Fig. 5a) [43]. When sun light irradiated on the DSSCs, the excited electrons induced the following chemical process as TiO2+xLi++xe−→LixTiO2 on the TiO2 anode, simultaneously the reaction of the cathode (LiCoO2 Li1−xCoO2 + xLi+ + xe−) released free electrons that flowed to the Pt electrode by an external circuit for combining with the excited holes. By using this hybrid structure, the system delivered a discharge capacity of38.89 µAh under the discharge density of 100 µA with the volt- age charged to 3 V in 8 min (right of Fig. 5a), and a total of 0.82% energy conversion and storage efficiency has been achieved. A simpler two-electrode system involving direct photo-oxidation of LiFePO4Nano crystals by light irradiation in the presence of the N719 dye as hybrid photo-cathode and Li metal as anode (left of Fig. 5b) [17]. However, it w a s regretful that the voltage plateau decreases below the 3.4 V from the 5th cycle (right of Fig. 5b). A novel strategy by using a photo electrode with a redox shuttle in the Li-LiFePO4 battery (Fig. 5c)[44]. According to the different potential among the VB of TiO2 nano photo catalyst, redox shuttle (I−/I3−) and LiFeO4 cathode, LiFePO4 can be oxidized into FePO4 during the photo assisted charging with the following three -steps reaction:

$TiO2+hv \rightarrow h++e-, h++3I- \rightarrow I3-+e-,$

$I3-+2LiFePO4 \rightarrow 2FePO4+3I-+2Li+.$

Due to the contribution o the photo voltage, the photo charging voltage of the LiFePO4 cathode was reduced to 2.78V(Fig.5d),which was lower than the discharge voltage of 3.41 V, resulting in 20% input electric energy saving(Fig. 5e).More importantly, this photo assisted rechargeable battery owned a fast light-respond(Fig.5f) and could be discharged at a stable voltage plateau of 3.41 V. The mentioned progress on the solar energy storage in Li- ion batteries has presented various photoelectric conversion systems. With the integration of dye sensitized photo electrode, the solar Li-ion battery can be self-charged and presents a total conversion and storage efficiency of 0.82% with the limited output voltage. Through employing the implied photo electrodes (such as TiO2 photo electrode and N719 dyed LiFePO4 photo electrode), the photo assisted charging Li-ion batteries deliver high discharge voltage and capacity with the limited total conversion efficiency.

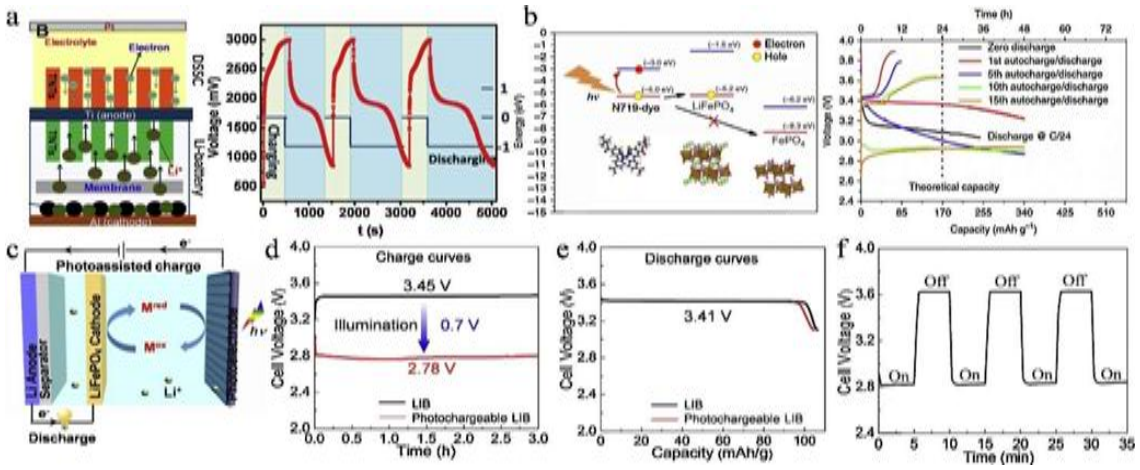


Fig.5.(a) Detailed structure and working principle of the integrated power pack system(left) and the corresponding cycling performance(right). (b) Energy band alignment of the photo-cathode components (left) and open circuit voltage and discharge curves of LiFePO4 film on ITO (right). (c) Schematic illustration of a photo assisted chargeable LIB (M: aredox shuttle). The charge (d) and discharge (c) curves of the photo assisted chargeable LIB (redline) and the LIB (black line). (f) Light-response of the charging voltage of a photo assisted chargeable LIB when switching the light from 'on' to 'off'.

Table-2: Solar Energy Storage in various Rechargeable batteries with the Internal Integration of Photo electrodes

Type	Photo electrode	Active material in anode/cathode	Separator	Discharge voltage	capacity	Tested cycling numbers	η1	η2	Ref.
Li-ion batteries	Dye sensitized electrode	TiO2 /LiCoO2	PE	2V	38.89 µA	3 cycles	0.82%		43
	N719 dye/LiFePO4	Li/LiFePO4		3.4V	340 mAh/g	15 cycles	0.06-0.08%		17
	TiO2	Li/LiFePO4	LISICON	3.41V	137 mAh/g	10 cycles		121%	44
Li-O2 Batteries	Dye sensitized electrode	Li/O2	Glassy fiber	2.8V		4 cycles		103%	16
	C3N4	Li/O2	Glassy fiber	2.74V	600 mAh/g	70 cycles		140%	52
Li-S Batteries	Cds/Pt	Li/S	LISICON	2.53V	792 mAh/g	10 cycles			61
Li-I Batteries	Dye sensitized electrode	Li/I	LISICON	3.3V	32600 mAh/L	25 cycles		120%	65
	α-Fe2O3	Li/I	LISICON	3.3V	192 mAh/g	22 cycles		95.40%	66
	TiO2	All vanadium redox cell	Nafion 117	0.8V	0.0042 µmol/h VO2+		12%		70
	TiO2	All vanadium redox cell	Nafion 117			50 cycles	45.60%		71

	α-Fe_2O_3	AQDS/K_4FeCN_6	Nafion 117	0.74V			0.05-0.08%		
Dual-liquid redox batteries	Dual silicon	AQDS/HBr	Nafion 115	0.78V	730 mAh/L	10 cycles	3.20%		
	Silicon solar cells	AQDS/BQDS	Nafion 212	0.41V	3500 mAh/L	10 cycles	1.70%		75
	Dye sensitized electrode	Li_2WO_4/LiI	LISICON	0.5V	0.0195 mAh/mL	10 cycles			
	Dye sensitized electrode	AB5-type hydrogen storage alloy/LiI	Modified Nafion 117	0.6V	26.7 mAh/g	20 cycles	1%		
	Dye sensitized electrode	Na_2S_4/NaI	CMI-7000	0.8V	240 μAh/Cm2	10 cycles	1.70%		76
	TiO_2	Na_2S_4/NaI	Nafion 117	0.83V	110 mAh/g	20 cycles		97%	
Other Batteries	TiO_2	WO_3/H_2O	LICGC	0.6V	10 mAh/g	10 cycles			
	TiN	$KFe[Fe(CN)_6]/H_2O$		0.8V	77.8 mAh/g	100 cycles			78

*η1: photo electric conversion and storage efficiency, η2: electric energy efficiency

Solar energy storage in Li-O2 batteries

The no aqueous Li-O2 battery shows appealing potential for large scale solar energy storage due to the paramount theoretical energy density (3550 Wh kg−1), which is several times higher than that of conventional Li-ion batteries (387 Wh kg−1) [45–5~1]. This is because lithium metal as the anode and oxygen gas as the cathode can be absorbed freely from the ambient air, thus greatly reduce the weight of Li-O2 battery. The use of inexhaustible oxygen gas as the cathode material is a strong advantage for its future development as well. Typically, a Li-O2 battery is composed of a porous carbon cathode, a lithium metal anode and a Li+ ion conductive electrolyte. In this battery, the fundamental electrochemical Reaction is:

$2Li+ + 2e− + O2 \leftrightarrow Li2O2$,

Therefore, the integration of solar energy with Li-O2 battery offers an inspirational strategy for simultaneous conversion and storage of solar energy. Photo-charged energy storage device by integrating a redox coupled TiO2-dye photo electrode into a non-aqueous Li-O2 battery [16]. During the charge process, the TiO2 photo electrode could drive the oxidation of discharge product (Li2O2), thus capturing solar energy and storing it as electrochemical energy (Fig. 6a). The light-response behavior was also a powerful evidence to support the photo-driven charge process (Fig. 6b), suggesting the effective utilization of solar energy. Utilizing solar energy allows Li-O2 battery to be charged at an input voltage of 2.8 V under illumination, which was much lower than that of a conventional Li-O2 battery (4.0 V). From the results of cyclability (Fig. 6c), made a further improvement with demonstrating the g-C3N4-CP photo catalyst could realize the direct photo-oxidation of Li2O2 without the unstable redox mediators (Fig. 6d) [52]. With this suitable design, the photo-charged Li-O2 battery exhibited much lower charge volt- age (2.0 V) and favorable cycling performance (Fig. 6d). The great voltage gain could contribute to a relatively high electric energy in more efficient solar energy utilization. From a broader perspective, these studies could be used as a general approach to design and develop other types of metal-ion batteries with the gas electrodes (such as Na-O2 batteries, Li-air batteries and Li-CO2 batteries) for solar energy storage.

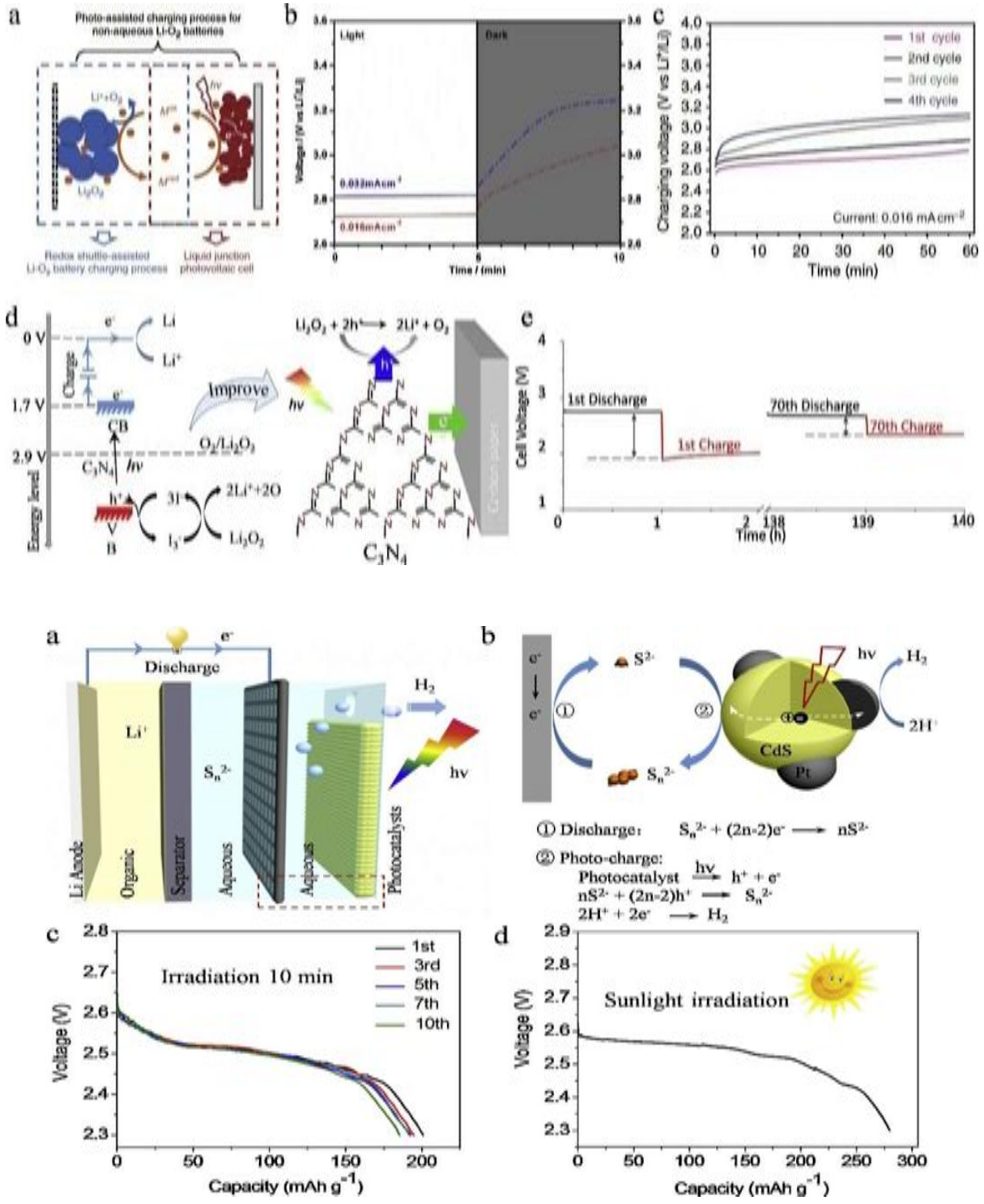


Fig 7(a) Schematic of the integration a photo catalyst into a Li-S battery for direct storage of solar energy (b) Photo-charge and discharge of solar-powered Li-S batteries. (c) The discharge curve saturate of 0.1mAcm−2 after 10 mini r radiation for ten cycles. (d) The discharge curve at a rate of 0.1mAcm−2 after 2h natural sunlight irradiation.

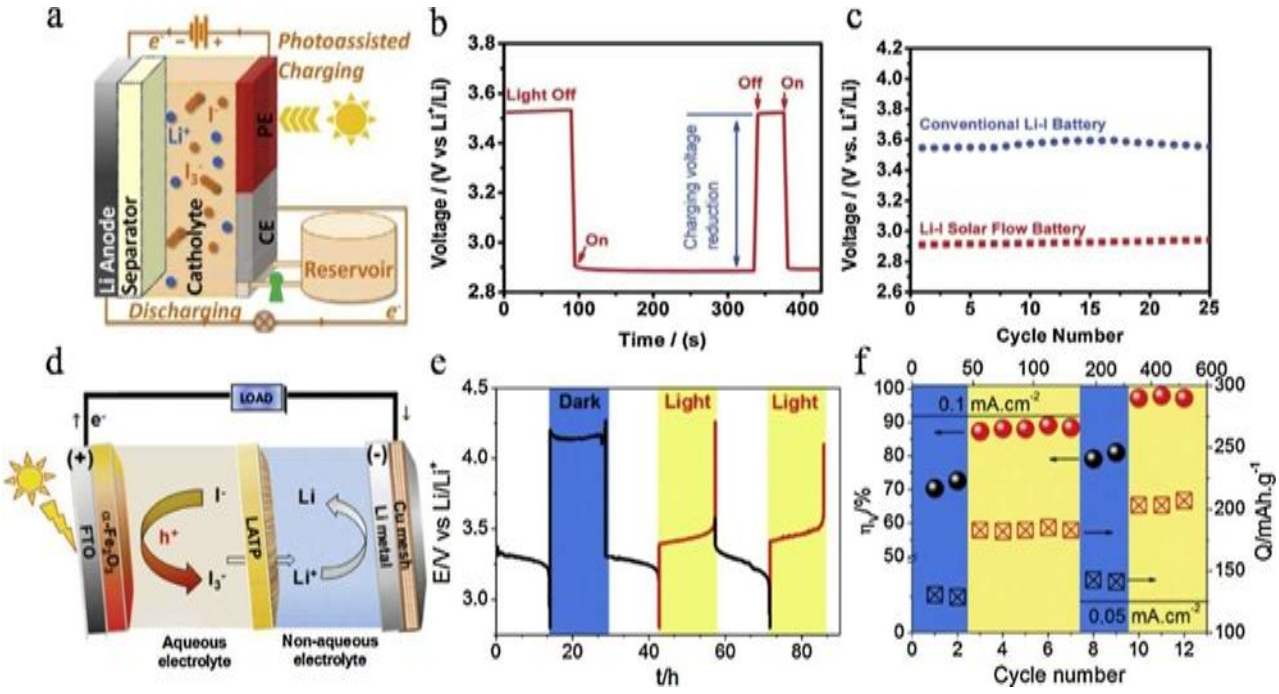


Fig 8(a) Schematic of a Li-ISFB with the three-electrode configuration (PE: a dye sensitized TiO2 photo electrode, CE: Pt counter electrode) and corresponding light response (b). (c) The initial charging voltages for 25 cycles of Li- I SFB. Reprinted with permission from Ref [83] (d) Illustrations of photo assisted charge process in Li-I cell. (e) Deep discharge-charge voltage profile under dark conditions for the first cycle (blue area) followed by illumination for the second and third cycles (yellow area). (f) Cycling performance of the voltaic efficiency (ηv) and capacity profiles at 0.1 and 0.05 mAcm−2.

Solar energy storage in Li-sulfur batteries

Among various electrochemical energy storage devices, Li- sulfur (Li-S) batteries hold great promise because sulfur is environmentally friendly and naturally resourceful and possesses a high gravimetric theoretical capacity of 1672 mAh g−1[53-60].Sulfur undergoes a series of structural changes as described by the redox reaction of S8 + 16 Li 8Li2S (2.15 V vs. Li/Li+) during the discharging and charging processes [55]. In the direct cap9ture and storage of solar energy into the hybrid Li-S battery with the configuration of Li/organic electrolyte (Fig. 7a) [61].The absorbed solar energy was used to oxidize S2− ions to poly sulfide ions, thus the charge process was achieved by photo-charging process without any electrical input (Fig.7b). After 2h light irradiation, the solar- driven chargeable Li-S battery exhibited a capacity of 792 mAh g−1. The good stability of solar-driven chargeable Li-S battery was demonstrated by the high capacity retention of 92.5% after 10 cycles (Fig.7c). Moreover, this device could also be operated under natural sunlight irradiation. The battery delivered a specific capacityof280mAhg−1under 2 h sunlight irradiation, implying its feasible application on future large-scale storage of solar energy (Fig. 7d). In the future, the development on a solar-powered rechargeable Li-S battery would be an important research direction in this field.

Solar energy storage in Li-iodine batteries

In order to attain the higher energy density (>250Whg−1) and high power density with the rapid charge and discharge rates, Li- iodine (Li-I) batteries as one of Li-redox batteries, combine the advantages of anode Li anode and iodine-based catholyte, and exhibit some unique characteristics such as the high-output volt- age

(3.05VversusLi+/Li), high theoretical capacity (211mAhg−1), and flexible operation. These attractive merits make the Li-I batteries considered as the next generation lithium-ion batteries for the long-range electric vehicles and large-scale energy storage [62-64]. The photo assisted charging concept for a solar- powered Li−I flow battery (Li-I SFB) by incorporation of a dye sensitized TiO2 photo electrode into a Li I redox flow battery (Fig. 8a) [65]. This feasible Li−I SFB with the integration of a dye sensitized TiO2 photo electrode displayed a fast light-response(Fig.8b) and a stable charging voltage plateau at 2.9V remained for 25 cycles (Fig. 8c), thus demonstrating energy savings up to 20% for conventional Li-I batteries. The dye sensitized photo electrode to the low-cost and simplified Seminar photo electrode, and demonstrated a photo assisted Li-I battery integrated with a hematite photo electrode (Fig. 8d) [66]. This photo assisted rechargeable battery exhibited electric energy efficiency around 95.4% with a charging voltage of 3.43 V (Fig. 8e) and remained the deep discharge charge cycles over 600 h without the remarkable performance decay and photo corrosion for hematite photo electrode (Fig. 8f). For realizing the efficient output of electric energy, the mentioned solar energy storage in Li-iodine batteries are mainly focused on the applications of a photo assisted charging strategy and the implication of photo electrode. Apart from the improvement for photo electrodes and separators, solar energy self- charging Li-I batteries would become one significant direction in the further development of this filed.

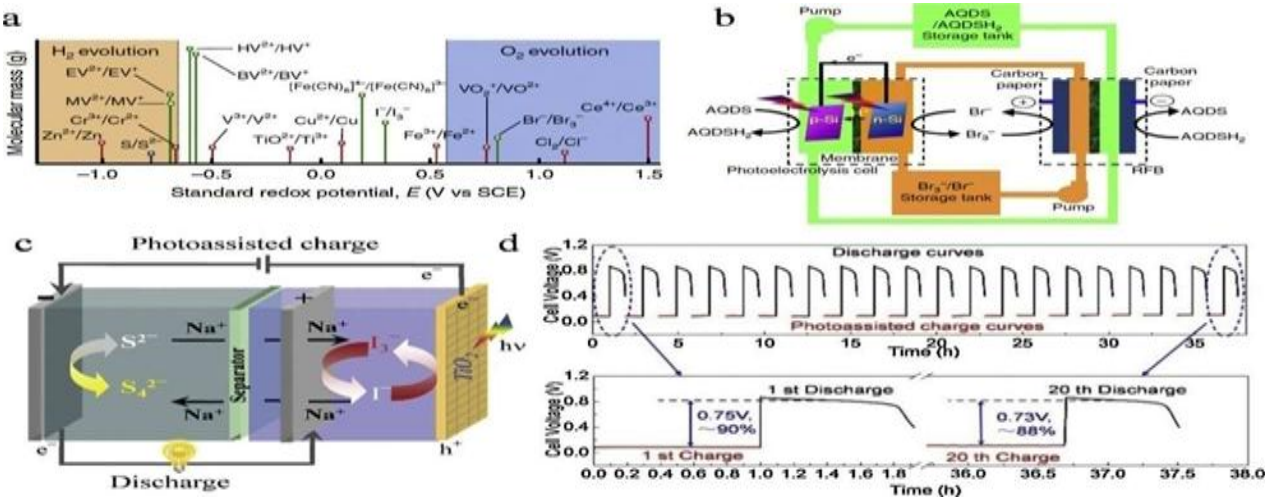


Fig 9. (a) Reduction potentials of the couples relative to the thermodynamic stability window of water at neutral pH (white region), SCE, standard calomel electrode.(b)Schematic configuration of a dual-silicon photo electro chemical cell in to a redox flow battery.(c) Schematic of a photo assisted rechargeable SPIB and the corresponding cycling performance (d).

Solar energy storage in dual-liquid redox batteries

In Difference with other rechargeable batteries employing the solid or gas materials on the active electrodes, the dual-liquid redox batteries enable to store electrical energy via two liquid redox-couple electrolytes (analyte and catholyte) for avoiding the concerns on the safety issues of metal anode (Li, Na and K etc.), and dual electrolytes can be stored in external reservoirs for different volumes. Through externally combining the electrodes and reservoirs by the powered pumps, the redox batteries can be flowed for the high-rate diffusion and are also called the redox-flow batteries [67, 68]. The potentials of common redox-couples are shown in Fig.9a [69]. The first solar battery was introduced in a redox battery with the Ag2S/Ag ad S/S2− respectively as anode and cathode and the CdSe photo electrode integrated in the catholyte in 1976 [14]. While sulfur-based solar redox batteries

are subject to the highly fabricated cost and toxicity of usable photo electrodes and the limited potential widows on redox- couples, the progress has been slowly made. Recently, all vanadium systems have been improved gradually and have reached the demonstrated stage for commercial fruitions. All-vanadium battery achieved a high Faradic efficiency of 95% by the integration of a TiO2 photo- electrode and peak incident-photon-to-current efficiency (IPCE) of 45% in solar energy storage [70, 71]. To improve the light absorption of TiO2, a TiO2/WO3 tandem electrode was studied in various vanadium redox electrolytes for obtaining the higher photo-response in all electrolytes [72, 73]. Although solar-powered all-vanadium batteries have been demonstrated to have a high incident-photon-to-current efficiency, the stable working voltage, large capacity, high-effective cycling performance and low-cost are still the significant objectives and inspires the further development on the new systems. A dual-silicon photo electrochemical cell into a quinine/bromine redox flow battery, that could be self-photo charged to 0.8 V and delivered a discharge capacity of 730 mAh L−1 with a higher voltage of 0.78 V (Fig. 9b) [74]. At the same time, this innovative work of self-photo charging by dual-photo electrodes may provide the guiding idea for highly efficient solar rechargeable devices. Other work has shown that the integrating regenerative silicon solar cells into the 9,10-anthraquinone-2,7-disulfonic acid (AQDS)/1,2-benzoquinone-3,5- disulfonic acid (BQDS) redox flow battery [75].Although, the output voltage is only 0.41 V, a higher capacity of 3500 Ah L−1 has been achieved after the directly Solar charging. This solar rechargeable battery could discharge at a discharge voltage of 0.6 V, and display a 88% capacity retention after the continuing 20 cycles. The dye- sensitized electrode and iodide–poly sulfide redox battery were hard to be combined. The assembled solar rechargeable redox battery displayed as table discharging voltage of 0.8V without putting the areal capacity of 240 μAh cm−2 [76]. In order to effectively utilize the high solubility of sodium iodide/poly sulfide redox species in the aqueous system, rechargeable sodium poly sulfide/iodine battery (SPIB) [15], which employed Na2S4 and NaI as the anolyte and catholyte respectively, and a TiO2 photo electrode integrated in to the catholyte for realizing the photo electric conversion in an aqueous system(Fig.9c).Due to the compensation of photo voltage, an ultralow photo assisted charging voltage of 0.08V was achieved, Resulting in the input electric energy of 90%. And this system remained good cycling stability after least 20 cycles with a stable discharging voltage of0.83 V (Fig. 9d).

The full aqueous photo assisted chargeable Na+-based redox battery paves the way toward practical application of low-cost and high-voltage photo chargeable batteries. At present, solar energy storage in dual-liquid redox batteries have employed the various redox species as analyte and catholyte, and achieved the high photoelectric conversion and storage efficiency. Therefore, the development on the low-cost, high activity and long-durability photo catalysts and the systems with wide voltage window would be two important directions in this field.

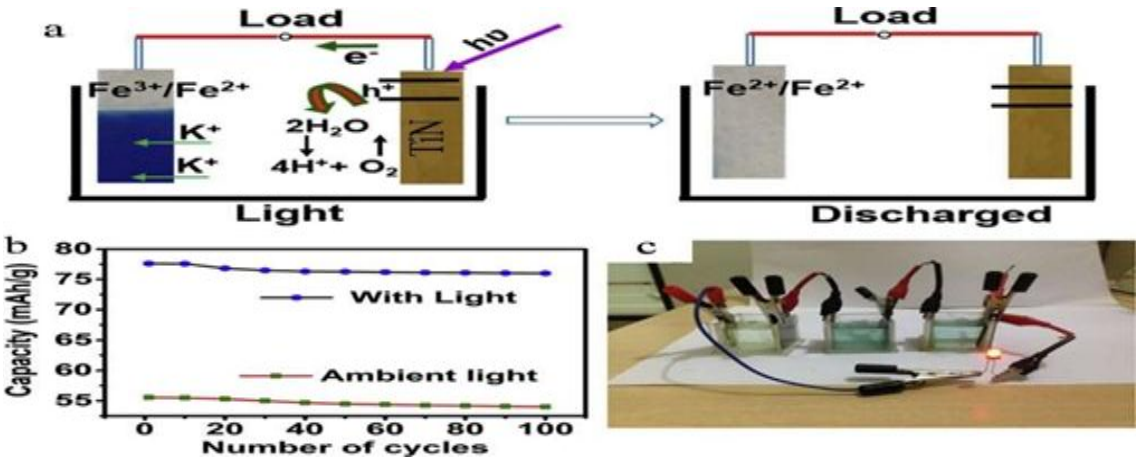


Fig 10 (a) Working mechanism of the chemically chargeable photo battery, the capacity vs cycle number and image of photo battery powering a LED (c).

Solar energy storage in other rechargeable batteries

Although the solar-energy storage has been investigated in the typical rechargeable batteries, there are still many of works contributing to other new-type rechargeable batteries, especially the distinct concepts have the enlightening significance. Nano crystalline MoO3 as photo catalyst and intercalation host materials for high energy density Li-ion batteries under the illumination, the photo charging mechanism was as shown in the following process:

MoO3 + hv MoO3∗+ e− + h+, 4 h+ + H2O 4H+ + O2, MoO3 + xA+ + xe− AxMoO3 [77]

An environmental friendly, namely- "solar water battery", based on a water oxidation reaction instead of the redox chemistry of a catholyte and the assembled battery could discharge at a stable voltage plateau of 0.6 V. Although the septic discharge capacitance of the battery was not so high using Tin as photo anode in a system (Fig. 10a) [78]. The battery could charge through chemical reaction and discharge at a high voltage of 0.8 V under illumination, especially it enabled to work using ambient light (Fig. 10b and c) and displayed the great utilization potentiality in the presence of indoor lighting and street light and soon. In general, most of solar energy storage in other batteries have integrated the photo electrode into aqueous solution for utilizing the excellent performance with photo catalytic water splitting. However, an external storage system for storing chemical fuels (H2 andO2) is necessary, which added the complexity of whole systems, and the confining volume of systems have delivered the limited discharge capacity and restricted the total photoelectric conversion. In the future, the new type hydrogen/oxygen storage materials and photo catalysts with high conversion efficiency and long cycle-life would be two important research aspects in this field. For taking a comprehensive comparison for various energy storage systems, the integrated solar batteries could be classified into the four types based on different active materials in the anode and cathode, and they include the solid, gas, catholyte and dual- liquid with anolyte and catholyte. Through the specific analyses and discussion for various electrochemical systems, the four-types batteries could be systematically compared in terms of the system characteristics, photo electrochemical performance and potential applications as displayed in Table3.

Solid as active material in cathode. For instance the solar energy storage in Li-ion batteries with solid cathode. In these systems, solid cathode is hard to be directly oxidized by photo excited holes, and there is the sluggish insertion/extraction of the ions in solid cathode. Gas as active material in cathode. For example, the solar energy storage in Li-O2 batteries. The solar powered Li-O2 battery can employ the low-cost and abundant O2 as active material, and the discharge product Li2O2 on the surface of photo electrode enables to be directly oxidized by photo excited holes. These batteries deliver the high discharge capacity and have the

great potentiality applied in open systems such as solar energy storage in Metal-Air battery. Catholyte in cathode. This type battery includes the solar-powered Li-S batteries and Li-I batteries, which combine the advantages of metal Li and catholyte.

Anolyte and catholyte respectively in anode and cathode. This dual-liquid system employs soluble redox species as active materials with avoiding the dendrites and safety issues of metal Li anode, and delivers the high photoelectric conversion and storage efficiency by taking advantage of the dual-liquid system and flowable design. In a word, solar-powered dual-liquid batteries enable to realize the highly effective utilization of solar energy into the large-scale electric systems.

Demand for solar with battery storage increases

Solar systems with energy storage are surging in popularity for a few reasons. The cost of solar batteries is decreasing; meanwhile, the prevalence of grid outages has climbed. There was a 30 percent increase in grid outages between 2009 and 2019, with a total of 37 million people affected in 2019. Blackouts can cause property damage, including frozen pipes and flooded basements. Hundreds of thousands of customers lost power in Wisconsin and Dallas County in 2019 due to severe thunderstorms, resulting in millions of dollars of damage. In California, intentional blackouts have been utilized to prevent wildfires. "While California has always led the country in solar deployment, the drivers behind that growth have shifted," said Austin Perea, a senior solar analyst for Wood Mackenzie. "This is primarily due to new-build solar demand and increased consumer interest in solar + storage solutions as a result of public safety power shutoffs that have left hundreds of thousands of utility customers in the dark. We look forward to discovering new solar energy trends that surface in 2020.

Table-3: Classification and Characteristics of integrated solar batteries.

Type of active material	Integrated solar batteries	Active materials	System Characteristics	Ref.
Solid	solar-powered Li-ion batteries	TiO2/LiCoO2 Li/LiFePO4	Extraction of the ions Solid material is hard to directly oxidized by the photo excited h+	17 43 44
Gas	solar-powered Li-O2 batteries	Li/O2	Low cost active material open systems with O2 input unmediated oxidization metal Li	16 52
Catholyte	Solar-powered Li-S batteries Li-L batteries	Li/S, Li/L	Flow able design soluble redox species Rapid charge transfer metal Li hazard special separator	61 65 66
Anolyte and Catholyte	Solar powered dual-liquid redox batteries	All vanadium, AQDS/BQDS Na2S4/Nal	Flow able design soluble redox species Rapid charge transfer Limited voltage of aqueous	15 70 71 74 75 76

CONCLUSION

The development of the advanced storage of solar energy in the rechargeable battery from solar energy to storable chemical energy among various batteries. The devices have been gradually developed in the optimized direction involving

the high conversion/storage efficiency of solar energy, large capacity with the high and stable working voltage, high energy and power density, long-term stability, cost effective and environmentally benign. For effectively harvesting the visible light, while the potential pollution and cost-issues limit their large-scale applications. While the easy evaporation and large volume of electrolytes and the needed extra- storage for H2, O2 or other products. Finally, reducing the entire cost of the solar-powered recharge-able batteries is benefit for promoting the commercial applications. The exploitation for the less-expensive and high durable separators is also a great challenge in the solar- powered rechargeable batteries. "While California has always led the country in solar deployment, the drivers behind that growth have shifted," said Austin Perea, a senior solar analyst for Wood Mackenzie. "This is primarily due to new-build solar demand and increased consumer interest in solar + storage solutions as a result of public safety power shutoffs that have left hundreds of thousands of utility customers in the dark". We look forward to discovering new solar energy trends that surface in 2020. However, there are some practical issues with the whole systems that need to be further addressed in the recent future. Significant research breakthroughs are still desired for efficient conversion and storage of solar energy in to electrical powers. The solar energy industry is part of a very dynamic market. Many factors including government policies, fossil fuel costs, solar energy technology advances, commodity prices, and even public awareness of the climate crisis impact solar energy deployment across the globe. What's in store for the next year? Let's explore some trends in solar energy to better understand what is on tap for 2020.

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